

CHAPTER NO 1

FUNDAMENTAL CONCEPTS AND DEFINITIONS

Energy is the quantitative property essential to life and all living organisms. Energy can be viewed as an ability to cause changes.

THERMODYNAMICS

Thermodynamics can be defined as the science of energy.

The name *Thermodynamics* originates from two Greek words;

Therme → Heat

Dynamis → Power

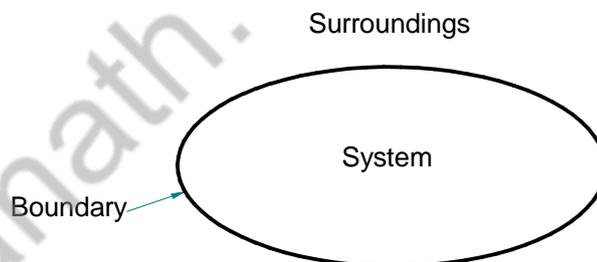
Thermodynamics is the science that deals with the relations between heat, work and those properties of the system that bears relation to heat and work.

THERMODYNAMIC SYSTEM

A *System* in thermodynamics is defined as a definite quantity of matter or a region in space upon which attention is focused for study.

Any mass or region outside/external to the system is called as the *Surroundings*.

The real or imaginary surface that separates the system from its surroundings is called as the *Boundary*.



System, surroundings and boundary

The boundary of a system can be fixed or movable. It is the contact surface shared by both the system and surroundings. The system and its surroundings together constitute the *Universe*.

Note: Mathematically, the boundary can neither contain any mass nor occupy any volume in the space, as it possesses zero thickness.

CLASSIFICATION OF THERMODYNAMIC SYSTEM

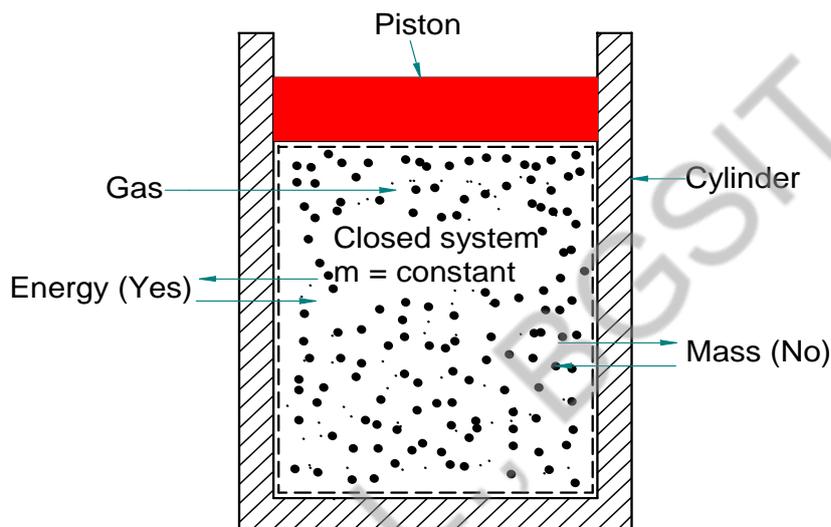
Based on whether a fixed mass or a fixed volume in space is chosen for study, the thermodynamic systems can be classified as

- i. Closed system and
- ii. Open system

Closed system

A *Closed System* (also called as *Control Mass*) is one which has a fixed amount of mass and no mass can cross its boundary; but energy in the form of heat or work, can cross the boundary and hence volume of a closed system may vary and as a result, its boundary is movable.

Example: Gas enclosed within a piston-cylinder device



Gas enclosed with in a piston-cylinder device

In a piston-cylinder device shown in the fig. If we want to know what happens to the gas enclosed when it is heated, we have to focus our attention on the gas and hence the gas is our system. The inner surface of the cylinder and lower/inner surface of the piston forms the boundary. It has been observed that no mass (i.e., gas) is crossing the boundary and hence it is a closed system. Energy either in the form of heat or as work may cross the boundary and part of the boundary (i.e., lower surface of the piston) may move. Everything external to the gas, including the piston and the cylinder is the surroundings.

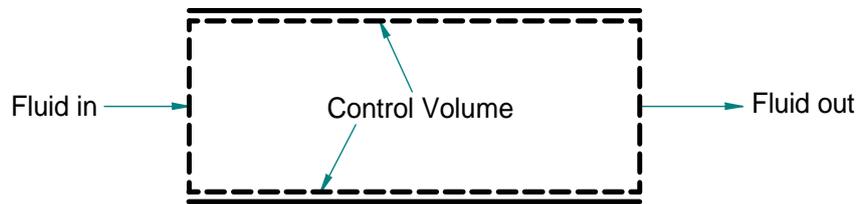
Open System

An *Open System* (also called as *Control Volume*) is one in which both mass and energy can cross the boundary of the open system. The region within the devices through which mass flow occurs such as a compressor, turbine, nozzle and tube selected as control volume. The boundaries of the control volume are called *Control Surface* can be real or imaginary.

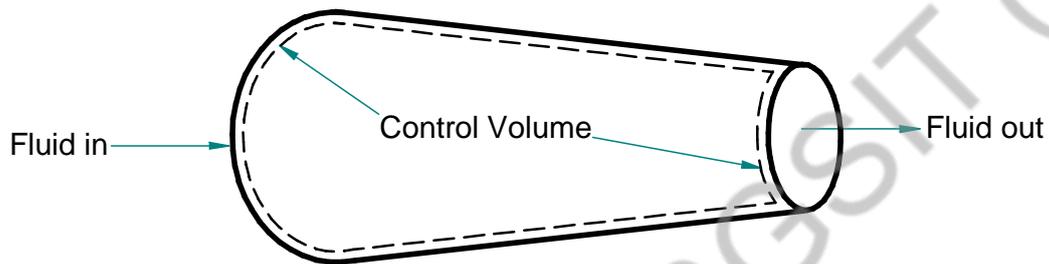
Example: Flow through tubes and nozzles

In case of flow through a tube or a nozzle, the inner surface of a tube or nozzle forms the real boundary and the entrance and exit areas form the imaginary boundary, as there

are no physical surfaces there. The mass (i.e. water) can enter and leave the imaginary boundary of the control volume/open system. Energy (i.e. kinetic energy possessed by moving water) as well as mass (i.e. water) can cross the boundary of the system.



(a)



(b)

Flow through (a) Tube and (b) Nozzle

SI No	Closed System	Open System
1	A certain quantity of matter is considered for study. Thus, a closed system has a Control mass.	A certain region is considered for study. This region is called as Control volume.
2	It is also called a non-flow system.	It is also called a flow system.
3	The system is surrounded by a real boundary which may be fixed or movable.	An open system is surrounded by a Control surface, which is a combination of real and imaginary boundaries.

Isolated System

An *isolated system* is a special case of closed system, in which neither an energy, nor as mass cross the boundary of the system. i.e., no exchange of energy or mass with the surroundings.

Example: Universe



MACROSCOPIC AND MICROSCOPIC APPROACHES/VIEWS

There are two points of view from which the behavior of the matter can be studied: Macroscopic and Microscopic.

SI No	Macroscopic Approach	Microscopic Approach
1	In this approach, certain quantity of matter is considered and gross or overall behaviour of all molecules taken into account.	In this approach, average behaviour of each and every molecule in the matter (system) is considered.
2	The knowledge of structure of the matter is not required.	The knowledge of structure of the matter is required.
3	This approach is called as Classical thermodynamics in the study of the thermodynamics.	This approach in the study of thermodynamics is called as Statistical thermodynamics.
4	Only few properties (co-ordinates) are sufficient to describe the matter completely.	In this approach, each and every molecule is to be described and each molecule requires 6 co-ordinates (3 space co-ordinates and 3 velocity components). Hence numbers of properties required are more.
5	The analysis of the system in this approach requires simple mathematical formulae as the no of molecules considered are less.	Since the number of molecules considered are more, more advanced statistical methods are required for analysis.

THERMODYNAMIC PROPERTIES OF A SYSTEM

Any observable/measurable characteristics of a system by which its physical conditions may be described is called a *Property*. A property has a definite value, when the system is in a particular state.

Examples: Pressure, volume, temperature, mass, velocity, viscosity, thermal conductivity and elastic resistivity, etc.

Classification of properties

Properties are classified based on dependability as

- a) Intensive and b) Extensive Properties

Intensive and Extensive Properties

Intensive properties are those that are independent of the mass of the system.

Examples: Pressure, temperature, density and velocity etc.

Generally lowercase letters are used for intensive properties (excluding pressure = P and temperature = T).

Extensive properties are those whose values depend on the size or extent of the system.

These properties depend on the mass of the system.

Examples: Total mass, total volume, total momentum and total energy etc.

Generally uppercase letters are used to denote extensive properties (excluding mass = m)

E (kJ)		$\frac{1}{2} E$	$\frac{1}{2} E$	Extensive Properties
m (Kg)		$\frac{1}{2} m$	$\frac{1}{2} m$	
v (m ³)		$\frac{1}{2} v$	$\frac{1}{2} v$	
T (°C)		T	T	Intensive properties
P (k Pa)		P	P	
ρ (Kg/ m ³)		ρ	ρ	
V (m/s)		V	V	

Extensive properties per unit mass are called *Specific Properties*.

Examples: Specific volume ($v = V/m$)

Specific total energy ($e = E/m$)

Working fluid

The matter contained within the system boundaries is called *working fluid*. It is used in thermodynamic devices as a medium for energy transport between the system and surroundings, while undergoing a thermodynamic process or cycle. A working fluid may be a gas, vapour, liquid or any non-reactive mixture of these constituents.

THERMODYNAMIC STATE, PATH, PROCESS AND CYCLE

State

The condition of the system at any instant of time as described or measured by its properties like pressure, temperature, specific volume, etc. is called as *Thermodynamic State* or simply a *State*.

OR

Each unique condition of a system is called a *State*.

$$\begin{array}{l}
 m = 2 \text{ kg} \\
 T_1 = 30^\circ \text{ C} \\
 V_1 = 10 \text{ m}^3
 \end{array}$$

State 1

$$\begin{array}{l}
 m = 2 \text{ kg} \\
 T_1 = 30^\circ \text{ C} \\
 V_1 = 15 \text{ m}^3
 \end{array}$$

State 2

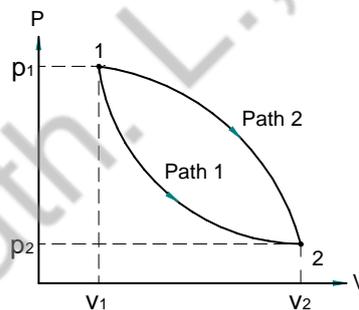
System at two different states

Process and Path

Any change that a system undergoes from one thermodynamic state to another is called a *Process*.

The series of states through which a system passes during a process is called the *Path* of the process.

Consider a system (i.e., a gas in a piston-cylinder device) at state 1 (at a particular position of the piston) where its conditions are described by P_1 , V_1 and T_1 . After expansion, the system reaches to new position or state 2 described by P_2 , V_2 and T_2 . The system may reach from state 1 to state 2 by a number of paths depending on the type of expansion.



Different paths with two states

CYCLIC AND NON- CYCLIC PROCESSES

Cyclic process/ Cycle

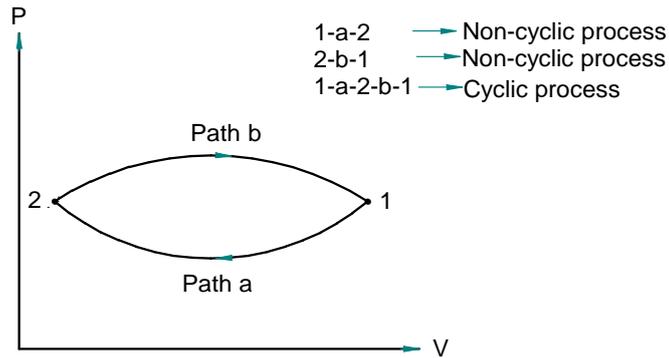
A system is said to have undergone a *Cycle/Cyclic Process*, if it returns to its initial state at the end of the process.

OR

A Cyclic process is one in which initial and final states of the system are identical (i.e. same) and hence no change in any property occurs during the completion of the process.

Non-cyclic process

A process is one in which initial and final states of the system are not same is called *non-cyclic process*.



Cyclic and Non-cyclic processes

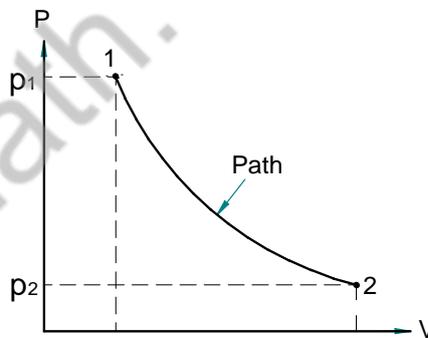
STATE DIAGRAM AND STATE POINT

State diagram

A diagram on Cartesian co-ordinates with any two independent properties are being represented along X-Y axes that represents the state of a system at different instants is called *State diagram*.

State Point

A point on a state diagram which indicates the state of the system at any given instant of time in terms of two independent properties selected for X and Y axes is called *State point*.



State diagram and state point

POINT FUNCTION AND PATH FUNCTION

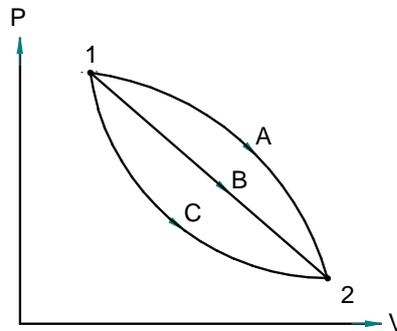
When a system undergoes a change from one state to another, the properties of the system also change, which depends only on end states and not on the path followed between these two states. These properties are called as *State functions* or *Point functions*.

The point functions can be represented by a point on any plot.

Examples: Pressure, temperature and volume etc.

A quantity whose value depends on the path followed during the process, not on the end points is called *Path function*.

Examples: Heat, Work etc.



Path function

A system can move from state 1 to state 2 by three different quasi-static paths. Area under each curve (path) represents the work involved in each process, which is not a function of end states of the process. But it depends on the path followed in reaching state 1 to state 2.

THERMODYNAMIC EQUILIBRIUM

A system is said to be in *thermodynamic equilibrium* if the temperature and pressure at all points are same.

A system is said to be in thermodynamic equilibrium with its surroundings, if it is in

a) Mechanical equilibrium b) Thermal equilibrium and c) Chemical equilibrium.

Mechanical equilibrium

A system is in *Mechanical equilibrium*, if the pressure in the system is same at all points and does not change with time.

Thermal equilibrium

A system is in Thermal equilibrium, if the temperature is same throughout the entire system and does not change with time.

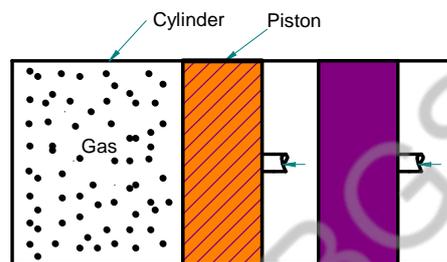
Chemical equilibrium

A system is in *Chemical equilibrium*, if its chemical composition is same throughout the entire system and does not change with time i.e., no chemical reactions occur.

QUASI-STATIC/QUASI-EQUILIBRIUM PROCESS

A process which proceeds in such a manner that the system remains infinitesimally close to an equilibrium states at all times is called a *Quasi-static* or *Quasi-equilibrium* process.

Consider a gas enclosed in a piston-cylinder device as shown in fig 1.20 is compressed slowly by adding very small weights on the piston. The piston moves slowly downwards. The molecules will have sufficient time to redistribute and there will not be molecule collision in front of the piston. As a result, the pressure inside the cylinder will always be nearly uniform and will rise at the same rate at all locations. Since equilibrium is maintained at all instants of time, it is a quasi-static process. Quasi-static processes are easy to analyze and infinite slowness is the characteristic feature of a quasi-static process.



Slow compression process (Quasi-equilibrium process)

TEMPERATURE AND EQUALITY OF TEMPERATURE

Temperature

The temperature can be defined as a measure of *hotness* or *coldness*.

Equality of temperature

When a body is brought in contact with another body at different temperature, the heat transfer takes place from body at higher temperature to a body at lower temperature until they attain same temperature and two bodies are said to be in thermal equilibrium.

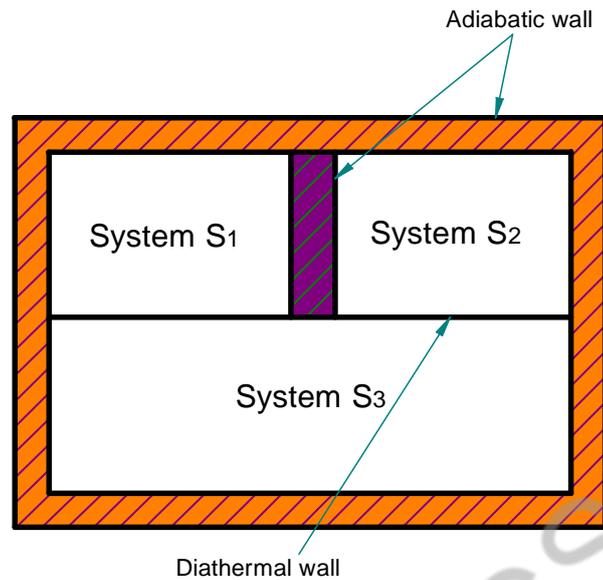
ZEROTH LAW OF THERMODYNAMICS

It states that *If two systems/bodies are in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.*

Consider two systems S_1 and S_2 which are separated by an adiabatic wall, and a third system S_3 is in communication (i.e., contact) with both systems as shown in figure 1.21.

Although, systems S_1 and S_2 are not in physical contact, they are in thermal equilibrium with a third system S_3 and hence S_1 and S_2 are also in thermal equilibrium with each other.

Zeroth law of thermodynamics serves a basis for the measurement of temperature by replacing the third system/body by a thermometer.



Three bodies in thermal equilibrium

MEASUREMENT OF TEMPERATURE

The measurement of temperature is carried out by establishing a thermal equilibrium between a system and the device used to measure the temperature.

A measurable property of a device that changes with change in temperature is called as *thermometric property* and the substance which shows the changes in its thermometric property with change in temperature is called *thermometric substance*.

Examples: Glass thermometer is a device, wherein, length of mercury changes with temperature.

TEMPERATURE SCALE

Temperature scales introduced so far are based on freezing point (i.e., ice point) and boiling point (i.e., steam point).

The temperature scale used in SI units is *Celsius scale*, wherein, ice point and steam points are assigned numerical values of 0°C and 100°C respectively.

The English system used the *Fahrenheit scale*, wherein, ice point and steam points are assigned numerical values 32°F and 212°F respectively.

Kelvin scale also called *absolute temperature scale* is related to the Celsius scale by

$$T(\text{K}) = T(^{\circ}\text{C}) + 273$$

Rankine scale related to Fahrenheit scale by

$$T(\text{R}) = T(^{\circ}\text{F}) + 460$$

The temperature scales on two-unit systems are related by

$$T(R) = 1.8T(^{\circ}C)$$

$$T(^{\circ}F) = 1.8T(^{\circ}C) + 32$$

THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE

International practical temperature scale used for calibration of temperature measuring instruments consists of following reproducible reference

Ice point

It is an equilibrium temperature of ice and air saturated water under one standard atmosphere.

Steam point

It is an equilibrium temperature of pure water and steam at one standard atmosphere.

Triple point

It is a state of equilibrium, where all three phases (solid, liquid and gas) of a substance co-exist simultaneously. The triple point of water is $0.01^{\circ}C$ ($271.16K$)

Boiling point

It is a state of equilibrium, where liquid and gas phases of a substance co-exist simultaneously. The boiling point of water is $100^{\circ}C$ ($373.15K$) at 1 standard atmosphere.

Melting point

It is a state of equilibrium, where solid and liquid phases of a substance co-exist simultaneously.

PROBLEMS:

- 1) The reading t_A and t_B of two Celsius thermometers A & B agree at the ice point and steam point and are related by the equation $t_A = L + M.t_B + N.t_B^2$. Between these two points L, M, N are constants. When both are immersed in an oil bath, thermometer „A“ indicates 55 and thermometer „B“ indicates 50. Determine the values of L, M, N and also find the reading on „A“ if „B“ reads 25.

Solution: As the two thermometers A and B agree at the ice point and steam point we have at Ice point: $t_A = 0$, $t_B = 0$

$$\begin{aligned}t_A &= L + \\ &M.t_B + \\ &N.t_B^2 = \\ &L + 0 + \\ &0 \\ &\mathbf{L = 0}\end{aligned}$$

At Steam point: $t_A = 100$, $t_B = 100$

$$t_A = L + M.t_B + N.t_B^2$$

$$100 = L + M.100 + N.100^2$$

$$\mathbf{M = 1 - 100.N}$$

when „A“ indicates 55, „B“ indicates 50

$$\text{hence } t_A = L + M.t_B + N.t_B^2$$

$$55 = 50.M + 2500.N$$

$$11 = 10.M + 500.N$$

Substituting for „M“ in the above equation we get

$$\mathbf{N = 1/500}$$

From equation $M = 1 - 100.N$

$$\mathbf{M = 6/5}$$

When thermometer „B“ reads 25, thermometer „A“

$$\text{read } t_A = L + M.t_B + N.t_B^2$$

$$t_A = 28.75$$

Thus when ‘B’ reads 25, ‘A’ reads 28.75

2). A temperature scale of certain thermometer is given by the relation $t = a \ln p + b$ Where a and b are constants and p is the thermometric property of the fluid in the thermometer. If at the ice point and steam point the thermometric properties are found to be 1.5 and 7.5 respectively what will be the temperature corresponding to the thermometric property of 3.5 on Celsius scale.

Solution. $t = a \ln p + b$ (Given) On Celsius scale:

Ice point = 0°C , and Steam point = 100°C

\therefore From given conditions, we have $0 = a \ln 1.5 + b$ (i)

and $100 = a \ln 7.5 + b$

...(ii) i.e., $0 = a \times 0.4054 + b$

...(iii)

and $100 = a \times 2.015 + b$...(iv)

Subtracting (iii) from (iv), we get $100 = 1.61a$ or $a = 62.112$

Substituting this value in eqn. (iii),

we get $b = -0.4054 \times 62.112 = -25.18$

\therefore When $p = 3.5$ the value of temperature is given by

$$\mathbf{t = 62.112 \ln (3.5) - 25.18 = 52.63^\circ\text{C.}}$$

CHAPTER NO 2

WORK AND HEAT

Mechanics definition of work: Work is done when the point of application of a force moves in the direction of the force. The amount of work is equal to the product of the force and the distance through which the point of application moves in the direction of the force. i.e., work is identified only when a force moves its point of application through an observable distance.

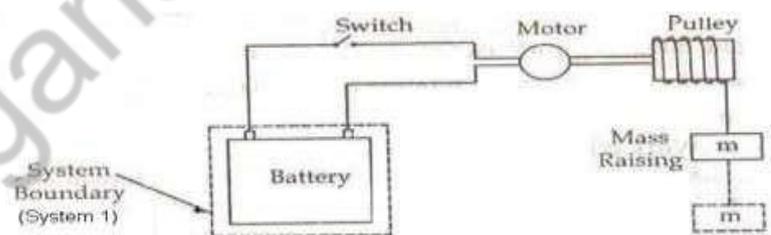
$$\text{Mathematically, } W = \int F \cdot dx$$

However, when treating thermodynamics from a macroscopic point of view, it is advantageous to tie in the definition work with the concepts of systems, properties and processes.

Thermodynamic definition of work: It is a kind of interaction that would occur at the system boundaries. It can be positive or negative. Definition of Positive work is said to be done by a system when the „sole effect“ external to the system could be reduced to the raising of a weight.

Comments: The word “sole effect” indicates that the raising of weight should be the only interaction between the system and surroundings in order to say that there is work interaction between the system and the surroundings. The phrase “external to the system” indicates that the work is a boundary phenomenon. The magnitude of work interaction depends upon the system boundary. This is illustrated with an example.

Figure 1: Equivalence of Current Work Interaction between the System and the Surroundings



For the two systems shown in figure, system (1) comprising battery alone has work interaction with the surroundings, whereas for system (2) which includes motor, weights etc. along with the battery, the work interaction is zero.

The word “could be reduced to” indicates that it is not necessary that weights should actually be raised in order to say that there is work interaction between the system and the surroundings. It is just sufficient to have an effect which is equivalent to the raising of weight.

Here an electrical storage battery constitutes system 1 whose terminals are connected to an electrical resistance coil through a switch. The circuit external to the battery constitutes the surroundings. When the switch is closed, the current flow through the coil, and the resistance (surroundings) become warmer and the charge of the battery (system) decreases. Obviously there has been interaction between the system and the surroundings. According to mechanics this interaction cannot be classified as work because there has been no action of force through a distance or of torque through an angle. However, as per thermodynamics concepts, the battery (system) does work as the electrical energy crosses the system boundary. Further, the electrical resistance can be replaced by an ideal frictionless motor pulley arrangement which can wind a string and thereby raise suspended weight. The sole effect, external to the system, is raising of a weight. As such interaction of battery with resistance coil is a work

Sign convention for Work:

- When work is done by the system, it is arbitrarily taken to be positive.
- When work is done on the system, it is arbitrarily taken to be negative.



P.dV work or Displacement Work:

Consider a system which contains a cylinder filled with a gas and a piston moving in the frictionless cylinder as shown in the figure. Let the piston move outward through a small distance „dx” in time interval „dt”. Since the piston moves only a small distance, the pressure acting on the face of the piston can be assumed constant. The infinitesimal (small amount) work done by the system is

$$\begin{aligned} \delta W &= \text{Force} \times \text{Displacement} \\ &= (P \times \text{Area of the piston} \times \text{Distance moved by the piston}) \\ &= (P \times A \times dx) \\ &= (P \times dV) \quad \{A \times dx = dV\} \\ \delta W &= P \times dV \end{aligned}$$

If the piston moves through a finite distance, the workdone by the piston is obtained by integrating the above equation between the initial and final state, thus we get

$$\int_1^2 \delta W = \int_1^2 P \times dV = W_{1-2}$$

If the process proceeds from state 2 to state 1 we can write

$$W_{2-1} = \int_2^1 \delta W = \int_2^1 P \times dV$$

This equation is applicable for i) Reversible or frictionless or quasistatic process ii) closed system iii) Effect due to viscous force, magnetic force, gravitational force and

electric force are negligible.

Point function and Path function:

1) Point function: A quantity say “x” that have a value at every point within its domain of definition or a quantity that depends on the states of the system but not on the path followed by the system is called point function. Its derivative is given by “dx” and its integral is

$$\int_1^2 dx = x_2 - x_1$$

Example: All intensive and extensive property

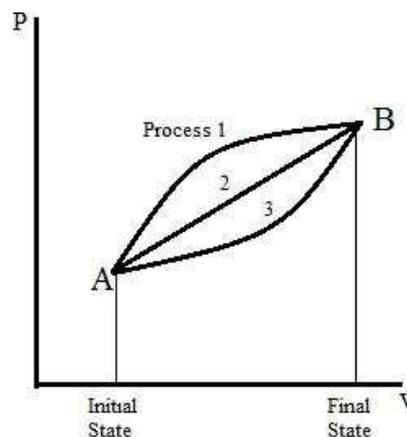
2) Path Function: A quantity say “y”, whose value depends on the mathematical path followed by the system to reach from initial state to the final state is called path function. It is an exact differential hence its derivative it is denoted by “dy”. Thus, we can write between two states 1 & 2

$$\int_1^2 \delta y = y_{1-2}$$

work is a path function:

Consider the P-V diagram as shown in the figure. It is possible to reach final state (state 2) from initial state (state 1) or vice versa by following different paths A, B & C. As the area under the curve represents the work for each process, it is evident that the amount of work involved in each process is dependent only on the path followed but not the end points. We can observe that the area under each curve of process is different hence we can conclude that work is a path function. Thus

$$\int_1^2 \Delta W = W_{1-2}$$



Other Modes of Work:

- **Shaft Work:** Consider an engine shaft rotated by means of an external force. The shaft undergoes an angular displacement when a constant torque „T” is applied to it
Shaft work is given by

$$\delta W = T \cdot d\theta$$

For finite changes shaft work is given by

$$\text{Shaft power} = P = \int^2 T \cdot d\theta = T \cdot m$$

$$W_{1-2} = \int T \cdot d\theta$$

Where m = Angular Velocity

• **Electrical Work:**

$$I = \frac{dC}{dt}$$

Where dC = Charge in coulombs that cross system boundary in time dt . Electrical work done by the flow of current is given by

$$\delta W = V \cdot dC$$

$$\delta W = V \cdot I \cdot dt$$

$$\text{Between two states } W_{1-2} = \int^2 VI.$$

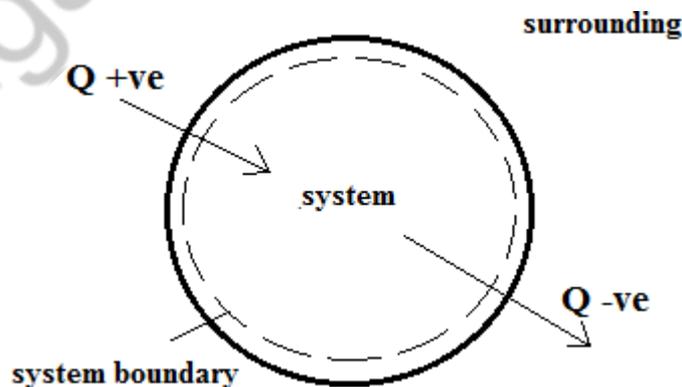
$$\text{Electrical Power} = P = V \cdot I$$

HEAT:

Heat is defined as the form of energy that is transferred between two systems or between system and its surroundings by virtue of a temperature difference.

Sign Convention for Heat:

- Heat transfer into the system is considered as **positive**.
- Heat transfer from the system is considered as **negative**.
- Unit of Heat transfer (Q) is **KJ**



Modes of Heat Transfer:

- 1) **Conduction:** Heat transfer due to direct contact between the elementary particles of a body that is molecules, atoms, free electrons.

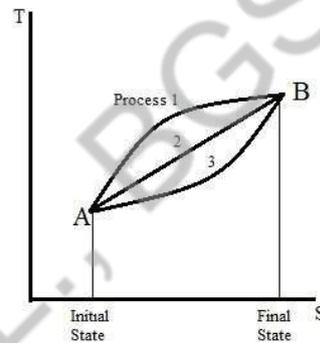
- 2) **Convection:** Heat transfer from one body to another by the moving particles of liquid, gas or loose solids during their relative motion in space.
- 3) **Radiation:** Heat transfer by electromagnetic waves through a medium which is transparent to thermal radiation. Fraction of the internal energy of a hot body is converted into radiant energy changing in the form of heat.

Heat is a Path Function:

Similar to work the amount of heat transferred from state 1 to state 2 depends on the path of the system. The area under different process is different hence the amount of heat transfer also varies. Hence for a quasi-static process heat transferred is written as

$$\int_1^2 \Delta Q = Q_{1-2} = \int_1^2 T \cdot dS$$

Where, S = it is an extensive property called Entropy



Comparison between work and heat:

Similarities:

- Both are path functions and inexact differentials.
- Both are boundary phenomenon i.e.; both are recognized at the boundaries of the system as they cross them.
- Both represent transient phenomenon; these energy interactions occur only when a system undergoes change of state i.e., both are associated with a process, not a state. Unlike properties, work or heat has no meaning at a state.
- A system possesses energy, but not works or heat.

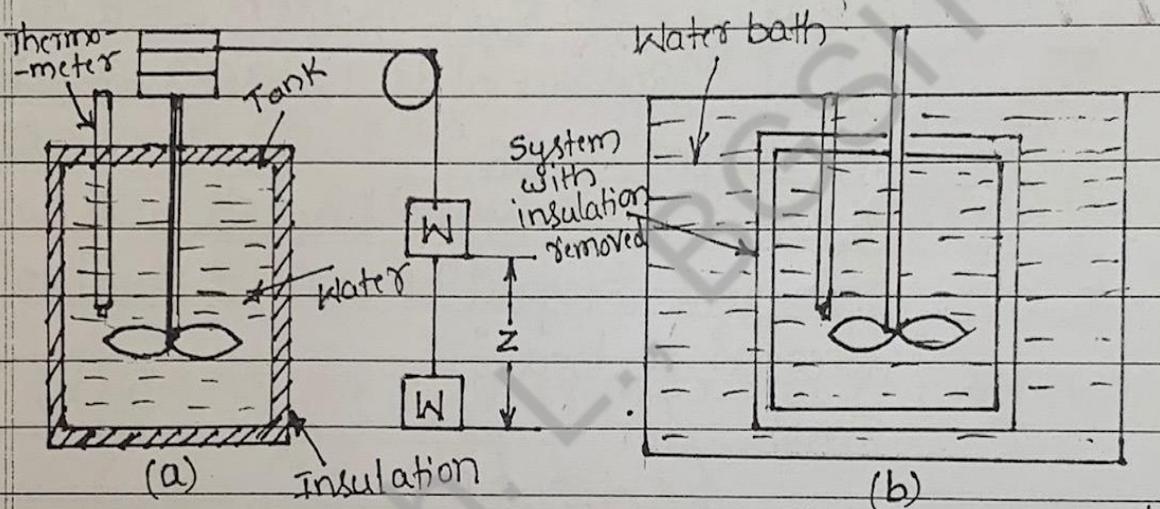
Dissimilarities:

- Heat is energy interaction due to temperature difference only; work is by reasons other than temperature difference.
- In a stable system, there cannot be work transfer; however, there is no restriction for the transfer of heat.
- The sole effect external to the system could be reduced to rise of a weight but in the case of a heat transfer other effects are also observed.
- Heat is a low grade energy whereas work is a high grade energy.

CHAPTER NO 3

FIRST LAW OF THERMODYNAMICS

IMP-2 Joule's experiment / First law of thermodynamic
for a closed system undergoing a cycle
Joule's made an experimental arrangement
is as shown in the figure 3-1 (a) and (b)



A known quantity of water taken in a rigid insulated tank as a system was stirred by a paddle wheel operated by a falling weights (Process 1). As a result of paddle work done on the system (i.e. water), there was a rise in the temperature of the system measured by a thermometer. The amount of work done was measured accurately as a product of weight and vertical distance through which the weight descends.

In order to restore the system to its original

(2)

state, the insulation from the tank was removed and then the whole system was kept in water bath as shown in the figure. The heat flows from the system to the water bath (process 2) till the system returns to its original temperature and thus restore the system to the same initial state and hence a system undergoes a cycle. During a complete cycle, there was a net work input to the system and net heat transfer from the system.

Joule conducted many similar experiments with different systems and various types of work. ~~the~~ Based on the experimental results, Joule conclude that "Whenever a system undergoes a cyclic process, the net work input to the system is directly proportional to the net heat output from the system" OR

"Whenever a system executes a cyclic process, the cyclic integral of work is equal to the cyclic integral of heat."

Thus,

$$\oint \delta W \propto \oint \delta Q$$

$$\oint \delta W = J \oint \delta Q$$

where J is a constant known as the Joule's constant or the mechanical equivalent of heat.

In S.I units, $J=1$, as heat & work are expressed in Joule

Therefore

$$\oint \delta W = \oint \delta Q$$

*VIMP 3.3 First law of thermodynamics for a closed system undergoing a change of state (or) First law of thermodynamics for non-cyclic process (or) Prove that Energy is a property of the system

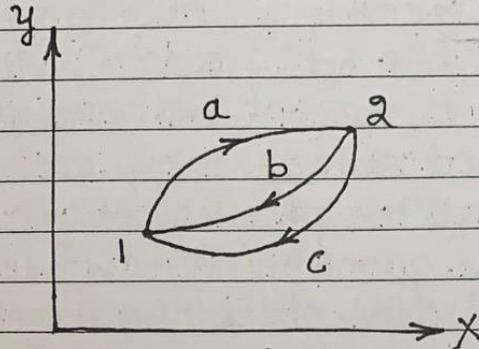


Fig 3.3 cyclic process

consider a closed system undergoing a change of state from state 1 to state 2 in two different cyclic processes 1-a-2-b-1 and 1-a-2-c-1 as shown in figure 3.3.

From the first law of thermodynamics, we have

$$\oint \delta Q = \oint \delta W$$

considering the cyclic process 1-a-2-b-1, we have

$$\int_{1a}^{\overset{2a}{2a}} \delta Q + \int_{2b}^{\overset{1b}{1b}} \delta Q = \int_{1a}^{\overset{2a}{2a}} \delta W + \int_{2b}^{\overset{1b}{1b}} \delta W \quad \text{--- (1)}$$

considering the cyclic process 1-a-2-c-1, we have

$$\int_{1a}^{\overset{2a}{2a}} \delta Q + \int_{2c}^{\overset{1c}{1c}} \delta Q = \int_{1a}^{\overset{2a}{2a}} \delta W + \int_{2c}^{\overset{1c}{1c}} \delta W \quad \text{--- (2)}$$

Subtracting the equation (2) from equation (1), we have

$$\int_{2b}^{\overset{1b}{1b}} \delta Q - \int_{2c}^{\overset{1c}{1c}} \delta Q = \int_{2b}^{\overset{1b}{1b}} \delta W - \int_{2c}^{\overset{1c}{1c}} \delta W$$

④

Rearranging

$$\int_{1b}^{2b} \delta Q - \delta W = \int_{1c}^{2c} \delta Q - \delta W \quad \text{--- (3)}$$

In equation (3), the quantity $(\delta Q - \delta W)$ is same for the process b and process c.

As b and c represent arbitrary processes between the state 1 and state 2, the quantity $(\delta Q - \delta W)$ is same for all the processes between states 1 and 2. Therefore, the quantity $(\delta Q - \delta W)$ depends only on the initial and final states of the system, but not on the path followed between the two states and hence it is a point function and it represents a change in some property of the system and this property is known as Energy of the system.

In general, equation (3) can be written as

$$\delta Q - \delta W = dE$$

$$\boxed{Q_{12} - W_{12} = E_2 - E_1}$$

where,

Q_{12} = Net heat transfer between the system and its surroundings during the process.

W_{12} = Net work transfer between the system and its surroundings during the process.

$(E_2 - E_1)$ = change in energy of the system during the process.

First law of thermodynamics to non-cyclic process states that "When a system undergoes a non-cyclic process, the difference between the net heat transfer during the process (Q) and the net work done (W) during the same process is always

equal to the change in the energy (ΔE) of the system.

3.4 classification of energy of a system

The energy in a system may be present in a variety of forms such as kinetic energy (KE), potential energy (PE) and internal energy (U) of a system. Then, the first law of thermodynamics equation becomes

$$Q_{12} - W_{12} = (KE_2 + PE_2 + U_2) - (KE_1 + PE_1 + U_1)$$

In most of the situations, the changes in the kinetic energy and potential energy is negligible and can be neglected. Thus, the first law becomes

$$Q_{12} - W_{12} = U_2 - U_1$$

Further, internal energy per unit mass is defined as the specific internal energy and is denoted by the symbol u

$$u = \frac{U}{m}$$

3.5. Enthalpy

The sum of internal energy and product of pressure and volume is called enthalpy of a substance (i.e. system).

$$H = U + PV, \text{ when pressure } P \text{ is constant.}$$

For 1 kg of a substance

$$h = u + Pv$$

where h = specific enthalpy of a substance

u = specific internal energy

v = specific volume of a substance

Enthalpy is also called total heat

3.8 Application of First Law of Thermodynamics to non-flow or closed system

1. Reversible constant volume (or Isochoric) process ($v = \text{constant}$)

During isochoric process, $v = \text{constant}$. Thus

$$W_{1,2} = \int_1^2 P dv = 0 \quad \text{as } dv = 0$$

According to First Law of Thermodynamics, we have

$$Q - W = U_2 - U_1$$

$$Q = U_2 - U_1$$

Also, we have

$$C_v = \frac{Q}{(T_2 - T_1)} \Rightarrow Q = C_v(T_2 - T_1)$$

Imp { For mass m of the substance

$$Q = (U_2 - U_1) = m C_v (T_2 - T_1)$$

a. Reversible constant pressure (or Isobaric) process ($P = \text{constant}$)

For an isobaric process, the work done

$$W_{1,2} = \int_1^2 P dv = P(v_2 - v_1)$$

Considering unit mass of a substance and applying first law of thermodynamics

$$Q - W = (U_2 - U_1)$$

$$Q - P(v_2 - v_1) = (U_2 - U_1)$$

$$Q = (U_2 + P_2 v_2) - (U_1 + P_1 v_1)$$

$$Q = (H_2 - H_1)$$

Also, $(H_2 - H_1) = m C_p (T_2 - T_1)$

Imp { $\therefore Q = (H_2 - H_1) = m C_p (T_2 - T_1)$

3. Reversible constant temperature (or Isothermal/hyperbolic) process ($Pv = \text{constant}$, $T = \text{constant}$)

For an isothermal process, the work done

$$W_{1,2} = \int_1^2 P dv = P_1 v_1 \ln\left(\frac{v_2}{v_1}\right) = P_1 v_1 \ln\left(\frac{P_1}{P_2}\right)$$

Considering unit mass of a substance and applying first law of thermodynamics

$$Q - W = U_2 - U_1$$

but $U_2 - U_1 = m C_v (T_2 - T_1)$ (i.e. Joule's law)

$$\therefore Q - W = 0 \quad (\because T \text{ is constant})$$

$$Q = W$$

Imp { $Q = P_1 v_1 \ln\left(\frac{v_2}{v_1}\right) = P_1 v_1 \ln\left(\frac{P_1}{P_2}\right)$

4. Reversible adiabatic process ($PV^\gamma = \text{constant}$)

During adiabatic process, no heat is transferred to or from the substance.

Considering unit mass of a substance and applying first law of thermodynamics

$$Q - W = (U_2 - U_1)$$

$$W = (U_1 - U_2) \quad (\because Q = 0)$$

For an adiabatic process, work done

$$W_{1-2} = \frac{P_1 V_1 - P_2 V_2}{(\gamma - 1)}$$

$$\text{Imp } \left\{ \therefore W = U_1 - U_2 = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} \right.$$

5. Polytropic process ($PV^n = \text{constant}$)

For a polytropic process, work done

$$W_{1-2} = \frac{P_1 V_1 - P_2 V_2}{n - 1} =$$

Applying the first law of thermodynamics,

$$Q - W = (U_2 - U_1)$$

For perfect gas $PV = RT$, then

$$W_{1-2} = \frac{R(T_1 - T_2)}{n - 1}$$

$$Q = (U_2 - U_1) + \frac{R(T_1 - T_2)}{(n - 1)}$$

$$Q = C_v(T_2 - T_1) + \frac{R(T_1 - T_2)}{(n - 1)}$$

$$Q = \frac{R(T_1 - T_2)}{(n - 1)} - C_v(T_1 - T_2)$$

$$\text{But, we have } C_v = \frac{R}{\gamma - 1}$$

$$\therefore Q = \frac{R(T_1 - T_2)}{(n - 1)} - \frac{R(T_1 - T_2)}{(\gamma - 1)}$$

$$Q = R(T_1 - T_2) \left[\frac{(\gamma - 1) - (n - 1)}{(n - 1)(\gamma - 1)} \right]$$

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$$Q = R(T_1 - T_2) \left[\frac{\gamma - 1 - n + 1}{(n-1)(\gamma-1)} \right]$$

$$Q = \frac{R(T_1 - T_2)(\gamma - n)}{(n-1)(\gamma-1)}$$

but $W = \frac{R(T_1 - T_2)}{(n-1)}$

Imp $\left\{ \begin{array}{l} \cdot \\ \cdot \end{array} \right. \left. \begin{array}{l} Q = \frac{(\gamma - n)}{(\gamma - 1)} W \\ \end{array} \right.$

SECOND LAW OF THERMODYNAMICS

1.

The First Law of thermodynamics states that during any cyclic process, the net work transfer is always directly proportional to the heat transfer and hence work and heat are mutually convertible one into another.

2.1 Limitations of 1st law of thermodynamics:

- 1). First law of thermodynamics does not place (impose) any restrictions on the direction of the process, but thermodynamic processes can proceed only in a certain direction, not in the reverse direction and first law does not ensure that the process will actually occur.

Examples :- (i) consider a cup of hot tea left in a room. Our experience says that, it eventually cools off after certain period. The amount of heat rejected by the tea is equal to the amount of energy gained by the room air, thereby satisfying the first law of thermodynamics. Now consider the reverse process; - The cold tea getting hotter in a room as a result of heat transfer from the room air. From the first law of Thermodynamics point of view, the reverse process is possible provided the amount of heat transfer from the room air is equal to the amount of heat transfer to the cold tea. But this process is impossible (never takes place) in nature.

- 2). An electrical work can be converted into heat energy through an electric heating element/stove, but its reverse process; supply of an amount of heat to this heating element will not generate any amount of electric work.

These experiments/examples indicate that there is a

definition direction in which heat transfer can take place.

3). When a cycle rider stops his cycle by applying friction brakes, the kinetic energy of the rotating (moving) wheel is absorbed by the brake blocks (shoes), whose temperature rises and hence the kinetic energy lost by the moving wheel is converted into heat energy. Consider the reverse process; the brake blocks are to cool off by supplying their heat energy to the cycle wheel to make it rotate, it does not occur in nature. This indicates that in a cyclic process, all the work can be converted into heat, but all the heat cannot be converted into work. Heat is a low grade energy and work is a high grade energy.

This inadequacy of 1st law of thermodynamics to identify whether a process can take place or not led to the statement of second law of thermodynamics.

2 Thermal Reservoir

Thermal or heat reservoir is a hypothetical body with an infinite heat capacity (heat capacity = Mass \times specific heat).

A thermal reservoir can supply or absorb any amount of heat without undergoing any change in its temperature.

Example :- Oceans, rivers, atmosphere, industrial furnace etc

A thermal reservoir which supplies heat energy is called heat source and which receives/absorbs heat energy is called heat sink.

The temperature of a thermal reservoir always remains constant.

2.3 Heat Engine

We know that the net amount of heat cannot be converted into work directly. The conversion of heat into work requires

Some special devices called heat engines.

IC engines, steam and gas turbines are the heat engines, but these are operated in mechanical cycles not in thermodynamic cycle, since the working fluid does not undergo a complete cycle.

Heat engines are classified into two types

- 1) Direct heat engine
- ii) Reversed heat engine.

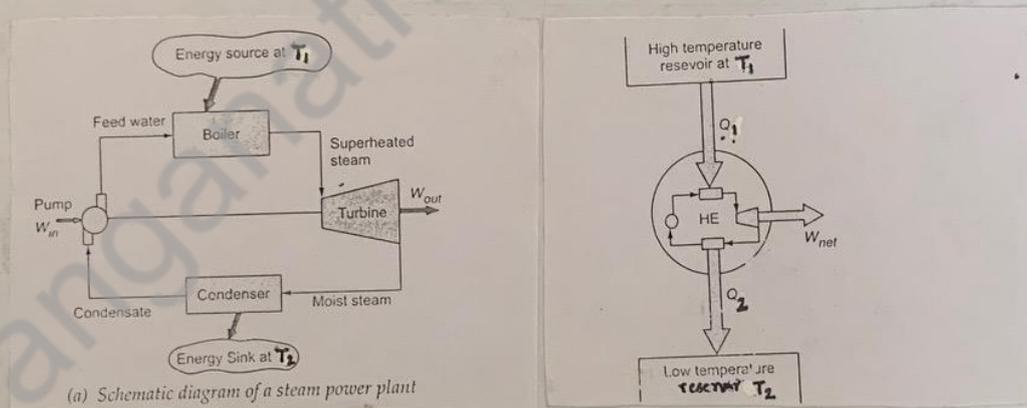
2.3.1a

Direct heat engine

A direct heat engine is a device (closed system) which operates in a cycle, receives the heat energy from a high temperature reservoir (source), converts part of it to work and rejects the remaining heat to a low temperature reservoir (sink)

Example :- steam power plant, closed cycle gas turbine plant etc.

The schematic diagram of a direct heat engine is shown below.



The heat engine receives heat " Q_1 " from a high temperature reservoir (source) at " T_1 ", converts part of heat supplied into useful net work " W_{net} " and rejects the remaining heat " Q_2 " to a

low temperature reservoir (sink) at T_2 .

For any cyclic heat engine, the net work is the difference between the heat supplied and heat rejected.

$$W_{\text{net}} = Q_1 - Q_2$$

2.3.2b Thermal efficiency of heat engine

The performance of a direct heat engine is measured by a parameter called 'thermal efficiency'.

In general, efficiency is nothing but ratio of what we want from the device to what we have to pay to achieve this.

Thermal efficiency is the ratio of desired output to the energy input.

In direct heat engine, the desired output is the net work W_{net} and energy input is the energy supplied Q_1 from high temperature reservoir.

Thermal efficiency is written as

$$\eta_{\text{th}} = \frac{\text{Net work output}}{\text{Energy input as heat}}$$

$$\eta_{\text{th}} = \frac{W_{\text{net}}}{Q_1}$$

$$\text{but } W_{\text{net}} = Q_1 - Q_2$$

$$\therefore \eta_{\text{th}} = \frac{Q_1 - Q_2}{Q_1}$$

$$\boxed{\eta_{\text{th}} = 1 - \frac{Q_2}{Q_1}}$$

Since both Q_1 and Q_2 are positive quantities/entities, the thermal efficiency of a heat engine is always less than unity (i.e. $< 100\%$).

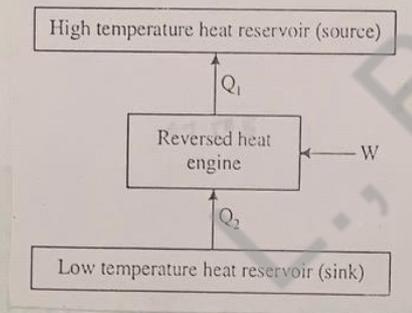
a.3.2a

Reversed heat engine

In case of a direct heat engine, if each and every equipment is made to operate in a reverse direction, it becomes a reversed heat engine.

A reversed heat engine is one which operates in a cycle, transfers heat from low temperature reservoir (sink) to a high temperature reservoir (source) with the aid of an external energy input.

Example: Refrigeration plant and heat pump plant



a.3.2b

Refrigerator:

A Refrigerator is a device, operating in a cycle, that maintains the body at lower temperature than its surroundings.

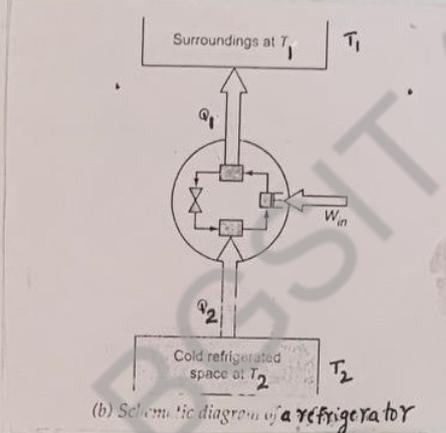
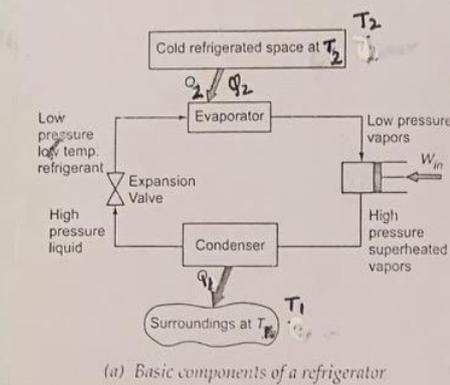
The working fluid in the refrigerator is called refrigerant.

The schematic diagram of a refrigerator (vapour compression cycle) is shown below.

The refrigerant evaporates by absorbing heat from the refrigerated space in the evaporator to keep it at low temperature.

The low pressure vapour enters the compressor, where it is compressed to very high pressure. In the condenser, the vapour refrigerant rejects its latent heat to the surroundings (atmospheric air). The

liquid refrigerant enters a capillary tube, where its pressure reduces drastically due to throttling effect. Then low pressure low temperature liquid refrigerant enters the evaporator & completes a cycle.



2.3.2c

Heat pump :-

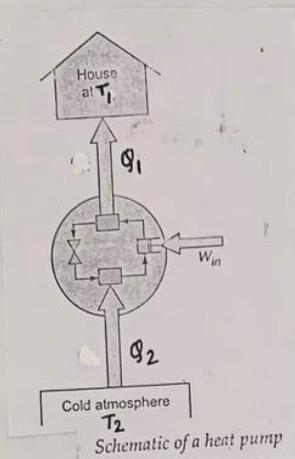
A heat pump is a device, operating in a cycle, that maintains a space at high temperature than the surroundings.

The heat pump absorbs the heat from the low temperature surroundings and supplies it to high temperature space at the cost of work input to the compressor.

The refrigerator and heat pump are operated on the same thermodynamic cycle, but they differ in their objectives.

If an ordinary refrigerator is placed in a window of a house with its evaporator open to outside and its condenser located in the room. then the refrigerator acts as a heat pump & it supplies heat to the room.

The schematic diagram of a heat pump is shown below.



Let Q_2 be the amount of heat be absorbed from the low temperature region and W_{in} be the work input, then the heat supply Q_1 to the room is the desired output for a heat pump.

2.3.2d Co-efficient of performance :-

The performance of a reversed heat engine (refrigerator & heat pump) is measured in terms of co-efficient of performance (COP) or Energy performance ratio (EPR).

The definition of COP depends on whether the reversed heat engine is used as a refrigerator or heat pump.

The COP of a refrigerator is defined as the ratio of heat transfer (Refrigerating effect) from the low temperature reservoir to the external energy input

$$(COP)_{Ref} = \frac{\text{Refrigerating effect}}{\text{Work input}} = \frac{Q_2}{W_{in}}$$

where $Q_2 \rightarrow$ heat removed from the low temperature region

$W_{in} \rightarrow$ Energy input in the form of work

but from first law for cyclic device, we have

$$W_{in} = Q_1 - Q_2$$

$$\therefore (COP)_{Ref} = \frac{Q_2}{Q_1 - Q_2}$$

$(COP)_{Ref}$ of a refrigerator may be greater than unity. i.e. the amount of heat removed from the refrigerated space may

be greater than the work input

COP of a heat pump is defined as the ratio of the heat transferred to the high temperature reservoir to the external energy input

$$(\text{COP})_{\text{HP}} = \frac{\text{Heat supplied}}{\text{Work input}}$$

$$(\text{COP})_{\text{HP}} = \frac{Q_1}{W_{\text{in}}}$$

where $Q_1 \Rightarrow$ heat supplied/transferred to high temperature reservoir

$W_{\text{in}} \Rightarrow$ work input

$$\therefore (\text{COP})_{\text{HP}} = \frac{Q_1}{W_{\text{in}}},$$

$$\text{but we have } W_{\text{in}} = Q_1 - Q_2 \Rightarrow Q_1 = W_{\text{in}} + Q_2$$

$$\therefore (\text{COP})_{\text{HP}} = \frac{Q_2 + W_{\text{in}}}{W_{\text{in}}}$$

$$(\text{COP})_{\text{HP}} = \frac{Q_2}{W_{\text{in}}} + 1$$

$$\text{but } \frac{Q_2}{W_{\text{in}}} = (\text{COP})_{\text{Ref}}$$

$$\therefore \boxed{(\text{COP})_{\text{HP}} = (\text{COP})_{\text{Ref}} + 1}$$

For the given values of Q_1 & Q_2 the $(\text{COP})_{\text{HP}}$ of a heat pump is always greater than the $(\text{COP})_{\text{Ref}}$ of a refrigerator by unity.

2.4 statements of second law of thermodynamics

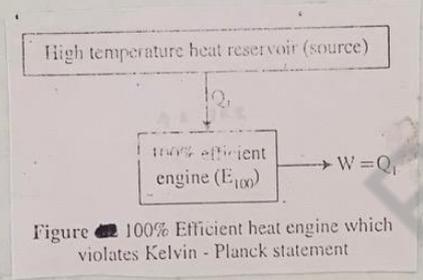
4. Kelvin-Planck statement :-

"It is impossible to construct an engine that operates in a thermodynamic cycle, produces no effect other than extract of

heat from a single temperature reservoir and do equivalent amount of work"

According to this statement, a heat engine cannot be 100% efficient, no heat engine can convert all heat supplied to useful work. It receives heat from high temperature reservoir and it must reject some amount of heat to a low temperature reservoir. The work done is the difference between heat supplied and heat rejection.

2.



2) Clausius statement :- It relates the working of the refrigerators and heat pumps.

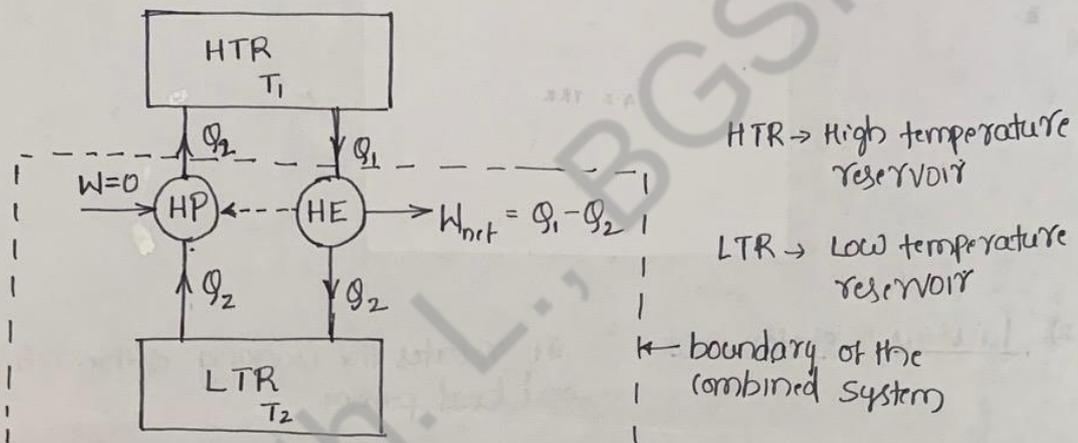
"It is impossible to construct a device that operates in a T.D cycle and produces no effect other than transfer of heat from a lower temperature body (cooler body) to high temperature body. (hotter body)

Heat energy flows from a hot body to a cold body & it can not flow by itself from a low temperature body to a high temperature body without addition of work. Refrigerators and heat pumps transfers heat from cold body to hot body at the cost of work input to their compressors.

3.5 Equivalence of Kelvin-Planck and Clausius statements

Though the Kelvin-Planck statement and the Clausius statement appear to be different, it can be shown that the two statements are equivalent in all respects; i.e. violation of Kelvin-Planck statement is violation of Clausius statement and vice-versa. This can be proved as follows

1. violation of Clausius statement implies the violation of Kelvin-Planck statement



In the LHS of the figure, a heat pump is transferring an amount of heat Q_2 from LTR (at T_2) to HTR (at T_1) without the aid (use) of an external work, thereby violating the Clausius statement.

On the RHS of the figure, a heat engine operates between the same reservoirs absorbing an amount of heat Q_1 from the HTR ($Q_1 > Q_2$) and rejecting an amount of heat Q_2 to LTR and does W_{net} amount of work. The engine alone does not violate the Kelvin-Planck statement.

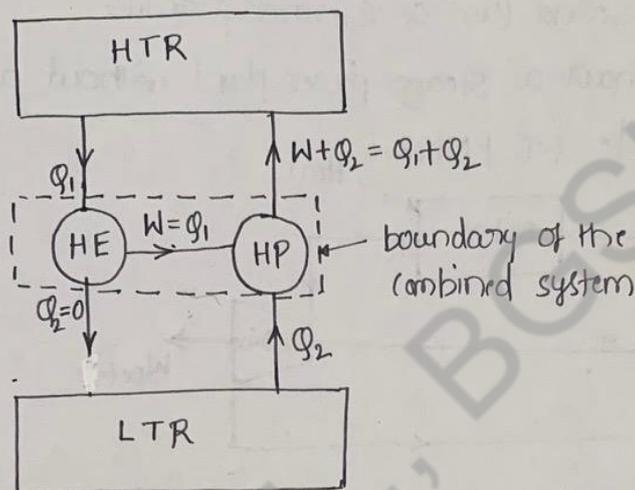
Since the heat Q_2 rejected by the heat engine is taken by the heat pump and rejects it to the HTR. Therefore LTR can be removed, as there is no net heat transfer to the LTR.

Now the heat engine, heat pump and LTR together considered as single device (system), the sole effect of this device is to receive $(Q_1 - Q_2)$ amount of heat from HTR and does equivalent amount of

work $[W=(Q_1-Q_2)]$ which violates Kelvin-Planck statement

∴ violation of Clausius statement violates the Kelvin-Planck statement.

2. violation of Kelvin-Planck's statement implies the violation of Clausius statement.



On LHS of the figure, the HE receives an amount of heat Q_1 from HTR and does an equal amount of work without rejecting heat to the LTR (i.e. $Q_2=0$); thus violating Kelvin-Planck's statement.

On the RHS of the figure, a heat pump operates between the same reservoirs, that receives Q_2 amount of heat from LTR & and transfer $(W+Q_2$ or $Q_1+Q_2)$ to HTR with the help of external work. Thus HP does not violate the Clausius statement.

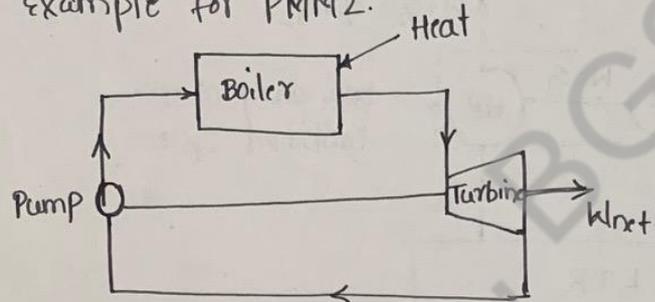
Now heat engine and heat pump together considered as a single device, the sole effect of this device is to transfer heat Q_2 from LTR to HTR by using the work developed by the heat engine (not from the external agency) thereby violating Clausius statement.

Hence violation of Kelvin-Planck statement is the violation of Clausius statement.

2.6 Perpetual motion machine of the second kind (PMM2)

A machine which absorbs the heat from a single thermal reservoir and converts this heat completely into work. The efficiency of such machine would be 100%. This machine is called perpetual motion machine of second kind (PMM2) which violates the second law of thermodynamics.

Fig shows a steam power plant without a condenser is an example for PMM2.



The condenser rejects more than half of the heat supplied as waste. The steam power plant where all the heat supplied into boiler will be converted to work by turbine & thus the power plant will theoretically have 100% efficiency. This PMM2 works in a cycle satisfying first law, but violates second law. Therefore it will not work, because heat is a low-grade energy and cannot be completely converted into work.

2.7 Carnot cycle or Carnot engine

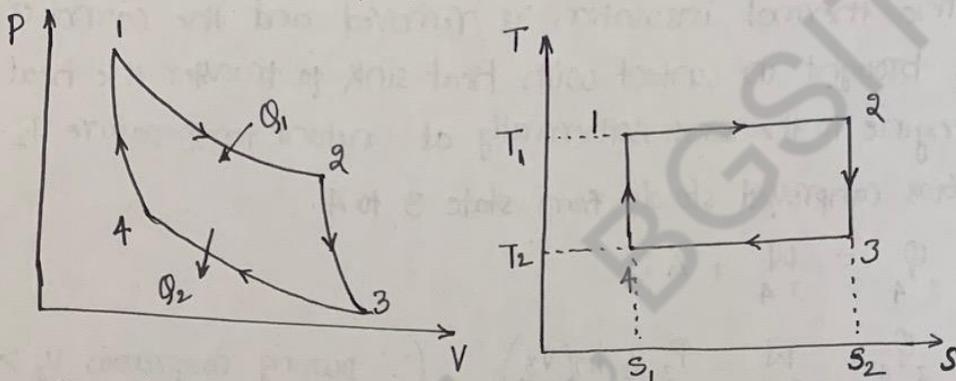
Carnot proposed an engine which works on a reversible cycle known as Carnot cycle or Carnot engine and the efficiency of which is maximum.

The Carnot cycle, also called reversible cycle, consists of following 4 reversible processes

1. Reversible isothermal expansion.
2. Reversible adiabatic (Isentropic) expansion
3. Reversible isothermal compression
4. Reversible adiabatic (Isentropic) compression.

The working of the engine is based on following assumptions.

1. All processes are frictionless
2. Any amount of heat transfer does not affect the temperature of source and sink.
3. The working substance is perfect gas.
4. The walls of the cylinder and piston ^{are} considered perfectly insulated.
5. The cylinder head is partially a very good conductor of heat and partially a perfect insulator.



1. Reversible Isothermal Expansion (Process 1-2)

The engine is brought in contact with a heat source and heat is added to the working medium (perfect gas) at constant temperature T_1 . The Gas expands slowly isothermally from state 1 to state 2

$$Q_{12} = W_{12} + \Delta U \quad (\text{From 1st law of thermodynamics})$$

but $\Delta U = 0$ for isothermal process

$$\begin{aligned} \therefore Q_1 = W_1 &= P_1 V_1 \ln\left(\frac{V_2}{V_1}\right) \\ &= mRT_1 \ln\left(\frac{V_2}{V_1}\right) \quad (\because PV = \frac{mRT}{\text{Gas}} \text{ for perfect}) \end{aligned} \quad \text{--- (1)}$$

2. Reversible adiabatic expansion (Process 2-3)

The engine is removed from the heat source and is thermally insulated. The Gas expands slowly until the temperature drops to T_2

2.7.1a Thermal Efficiency of a Carnot (Reversible) heat engine.

The thermal efficiency of any heat engine can be calculated as

$$\eta_{th} = \frac{\text{Net Work done}}{\text{Heat supplied}} = \frac{W_{net}}{Q_1}$$

For a cyclic heat engine, $W_{net} = Q_1 - Q_2$

$$\therefore \eta_{th} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

From eqn (1) & (3) for Carnot heat engine

$$\eta_{th} = 1 - \frac{MRT_2 \ln(V_3/V_4)}{MRT_1 \ln(V_2/V_1)}$$

considering the isentropic process 2-3

$$P_2 V_2^\gamma = P_3 V_3^\gamma$$

$$\frac{P_3}{P_2} = \left(\frac{V_2}{V_3}\right)^\gamma \quad \text{--- (*) (1)}$$

Also we have

$$\frac{P_2 V_2}{T_2} = \frac{P_3 V_3}{T_3}$$

, but $T_2 = T_1$ & $T_3 = T_2$
(From Carnot cycle)

$$\frac{T_1}{T_2} = \frac{P_2 V_2}{T_1} = \frac{P_3 V_3}{T_2}$$

$$\frac{P_3}{P_2} = \frac{T_2 V_2}{T_1 V_3} \quad \text{--- (***) (2)}$$

From eqns * & **

$$\left(\frac{V_2}{V_3}\right)^\gamma = \left(\frac{T_2}{T_1}\right) \frac{V_2}{V_3}$$

$$\therefore \frac{\left(\frac{V_2}{V_3}\right)^\gamma}{\left(\frac{V_2}{V_3}\right)^1} = \frac{T_2}{T_1}$$

$$\therefore \frac{T_2}{T_1} = \left(\frac{V_2}{V_3} \right)^{\gamma-1} \quad \text{*** (3)}$$

Similarly for isentropic process 4-1

$$P_4 V_4^\gamma = P_1 V_1^\gamma$$

$$\therefore \frac{P_4}{P_1} = \left(\frac{V_1}{V_4} \right)^\gamma \quad \text{**** (4)}$$

Also we have

$$\frac{P_4 V_4}{T_4} = \frac{P_1 V_1}{T_1} \quad \text{but } T_4 = T_2$$

$$\therefore \frac{P_4 V_4}{T_2} = \frac{P_1 V_1}{T_1}$$

$$\therefore \frac{P_4}{P_1} = \frac{V_1 T_2}{V_4 T_1} \quad \text{***** (5)}$$

From eqns *** & *****

$$\left(\frac{V_1}{V_4} \right)^\gamma = \left(\frac{V_1}{V_4} \right) \left(\frac{T_2}{T_1} \right)$$

$$\frac{\left(\frac{V_1}{V_4} \right)^\gamma}{\left(\frac{V_1}{V_4} \right)^1} = \frac{T_2}{T_1}$$

$$\therefore \left(\frac{V_1}{V_4} \right)^{\gamma-1} = \frac{T_2}{T_1} \quad \text{***** (6)}$$

From eqns (3) & (6), we have

$$\frac{V_2}{V_3} = \frac{V_1}{V_4} \Rightarrow \boxed{\frac{V_2}{V_1} = \frac{V_3}{V_4}}$$

\therefore

$$\eta_{th} = 1 - \frac{MRT_2 \ln(V_3/V_4)}{MRT_1 \ln(V_3/V_1)}$$

$$\eta_{th} = 1 - \frac{T_2}{T_1}$$

The efficiency of a Carnot engine is independent of the working substance. It depends on the source and sink temperatures. The efficiency

becomes maximum when sink temperature becomes zero (ie $T_2 = 0$), but it is not possible, as it violates the Kelvin-Planck's statement. Any value of efficiency can be obtained when $(T_1 - T_2)$ will have a definite value and efficiency is greater when the temperature difference is higher.

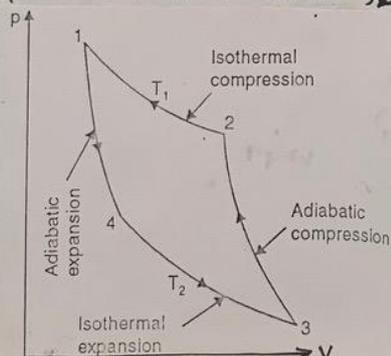
2.8 Reversible heat engine

A heat engine working between two constant but different temperature heat reservoirs is said to be reversible, if its efficiency when operating as a direct heat engine is equal to the reciprocal of its Co-efficient of performance when operating as a heat pump between same heat reservoirs

$$\text{ie } \eta_R = \frac{1}{(\text{COP})_{\text{H.P.R.}}}$$

2.9 Reversed Carnot cycle/engine

Since the Carnot cycle is reversible, its directions can be reversed, then it is operated as a reversible heat pump or a reversible refrigerator. The cycle undergoes same path and processes, only their directions are changed. This cycle requires work input W_{net} to transfer heat Q_2 from LTR to HTR.



2.13 Show that absolute zero temperature cannot be achieved

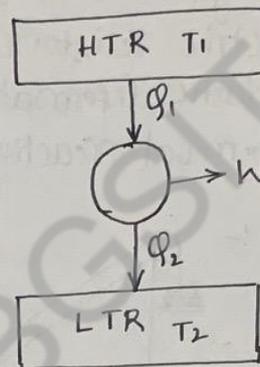
Consider a Carnot engine working between temperature limits T_1 and T_2

According to Carnot's third theorem,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\text{Efficiency } \eta = 1 - \frac{Q_2}{Q_1}$$

$$\eta = 1 - \frac{T_2}{T_1}$$



Now if we consider that temperature T_2 is equal to zero (i.e. absolute zero), the heat rejected Q_2 becomes zero

and the Carnot engine will have 100% efficiency. But this violates 2nd law of T.D. Thus heat rejected can never be zero and thus absolute zero can never be attained

2.14

Third law of thermodynamics

"The temperature of a system can not be reduced to zero in a finite number of processes"

2.15

Reversible and irreversible processes

A Reversible process is defined as a process that can be reversed without leaving any trace on the surroundings. i.e. both the system and surroundings are returned to their initial states at the end of the reverse process. This is possible only if the net heat and net work exchange between the system and surroundings is zero for the combined (original & reverse) process.

Processes that are not reversible are called irreversible processes.

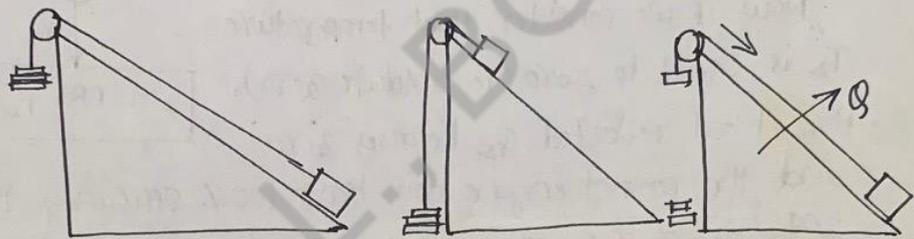
2.16 Irreversibilities or Factors that render a process

Irreversible:-

The factors that cause a process to be irreversible are called irreversibilities. They are

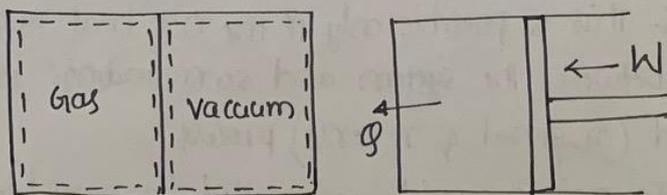
1. Friction.
2. unrestrained expansion
3. Heat transfer through finite temperature difference
4. Mixing of two different substances
5. Electric resistance
6. Inelastic deformation of solids and
7. Chemical reactions.

Friction:-



Consider a system comprising of a block and an inclined plane. Let the block is pulled up by lowering the weights, W & thus doing work on the system. Some of this work is required to overcome the friction between the block and plane. Let the system can be brought back to its initial state (position) by transferring the heat generated due to friction to the surroundings. Since there is a change in the system and surroundings, it is not a reversible process & hence friction makes the process irreversible

unrestrained expansion:-

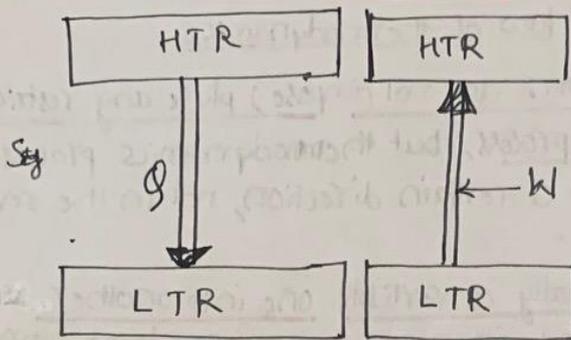


consider a system in which gas is separated from vacuum by a membrane. Let the membrane breaks so that entire vessel is filled with gas. The only

way to bring back the system to its initial condition is to compress the gas during which work is done on the system and the heat

generated during compression is transferred from the gas to the surroundings. work and heat transfer involve a change in the surroundings and is not returned back to its initial state. The process is irreversible and this process is termed as unrestrained expansion.

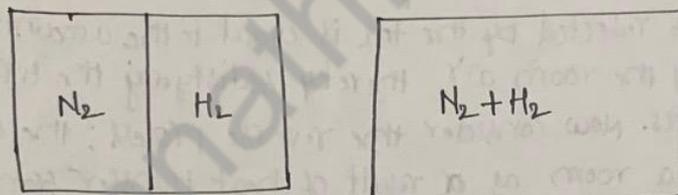
Finite temperature difference :-



consider a system in which heat is transferred from HTR to LTR. the only way to bring system back to its initial condition is by refrigeration, which requires certain amount of work to be done on the system and some heat

transfer from the system to the surroundings. Because of the work and heat transfer, the surroundings are not restored to its initial state indicating that ~~finite~~ heat transfer through finite temperature difference is an irreversible process.

mixing of two different substances



consider a system in which two different gases are separated by a membrane. Let the membrane breaks and homogeneous mixture of N_2 and H_2 fill the entire volume. This is a special case of unrestrained expansion, for each gas undergoes an unrestrained expansion, as it fills the entire system and hence the ~~system~~ process is irreversible.

Entropy

Entropy is an extensive property of the system whose change is given by $ds = \frac{dq_r}{T}$

Entropy is a function of a quantity of heat which shows the possibility of conversion of that heat into work. The increase in entropy is small when heat is added at high temperature and is greater when heat is added at lower temperature. Thus, for maximum entropy, there is minimum availability of for conversion into work and for minimum entropy, there is maximum availability for conversion.

Entropy can be considered as a measure of disorder.

Clausius theorem

The Clausius theorem states that the algebraic summation of all $\frac{\delta Q}{T}$ is always zero for a reversible cycle.

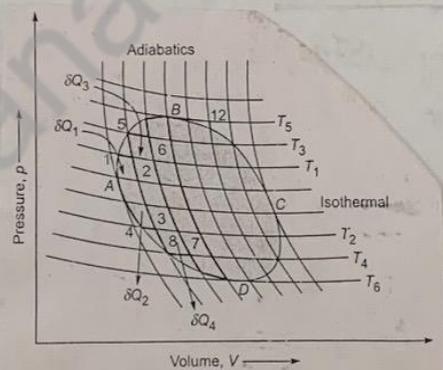


Fig. 7.3 A reversible cycle approximated by a number of small Carnot cycles

Consider a smooth curve representing a reversible cycle. The original reversible cycle is divided into no. of small Carnot cycles by drawing large no. of reversible adiabatic and reversible isothermal lines.

For a small Carnot cycle 1-2-3-4, δQ_1 is the heat supplied at constant temperature T_1 and δQ_2 is the heat rejection at constant temperature T_2 .

According to Carnot's third theorem

$$\frac{\delta q_1}{T_1} = \frac{\delta q_2}{T_2}$$

consider the sign convention (ie +ve for heat addition) and -ve for heat rejection)

$$\frac{\delta q_1}{T_1} = - \frac{\delta q_2}{T_2}$$

$$\frac{\delta q_1}{T_1} + \frac{\delta q_2}{T_2} = 0$$

similarly for small Carnot cycle, 5-6-7-8, the transfer of heat at δq_3 at T_3 and δq_4 at T_4 .

$$\frac{\delta q_3}{T_3} + \frac{\delta q_4}{T_4} = 0 \quad \text{and so on.}$$

For all small Carnot cycles, approximating a reversible cycle

$$\left(\frac{\delta q_1}{T_1} + \frac{\delta q_2}{T_2}\right) + \left(\frac{\delta q_3}{T_3} + \frac{\delta q_4}{T_4}\right) + \dots = 0$$

or $\oint \frac{\delta q}{T} = 0$ For reversible cycle

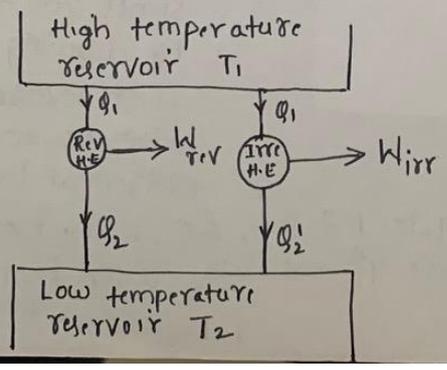
This is Clausius theorem.

Clausius inequality :-

The Clausius inequality states that when a system is undergoing a cycle, the cyclic integral or summation of

$$\frac{\delta q}{T} \leq 0.$$

The Clausius inequality is true for all types of cycles, reversible and irreversible.



consider reversible and irreversible heat engines, both operating between a high temperature reservoir (HTR) at T_1 and low temperature reservoir (LTR) at T_2 . The amount of heat supplied q_1

(3)

to both engines is same. The reversible engine rejects Q_2 and does work W_{rev}

consider a reversible heat engine

$$\begin{aligned}\oint \left(\frac{\delta Q}{T}\right)_{rev} &= \int \frac{\delta Q_1}{T_1} - \int \frac{\delta Q_2}{T_2} \\ &= \frac{1}{T_1} \int \delta Q_1 - \frac{1}{T_2} \int \delta Q_2 \\ &= \frac{Q_1}{T_1} - \frac{Q_2}{T_2}\end{aligned}$$

According to Carnot's third theorem

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$\therefore \oint \left(\frac{\delta Q}{T}\right)_{rev} = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \quad \text{--- (1)}$$

Now consider an irreversible heat engine, delivering less work W_{irr} than the reversible engine. Thus it rejects more heat Q_2'

$$\therefore Q_2' > Q_2$$

$$\text{i.e. } Q_2' = Q_2 + Q_{\text{difference}}$$

then

$$\oint \left(\frac{\delta Q}{T}\right)_{irr} = \int \frac{\delta Q_1}{T_1} - \int \frac{\delta Q_2'}{T_2}$$

$$\oint \left(\frac{\delta Q}{T}\right)_{irr} = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} - \frac{Q_{\text{diff}}}{T_2}$$

$$\text{but } \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \quad (\because \text{Eqn 1})$$

$$\text{Thus } \oint \left(\frac{\delta Q}{T}\right)_{irr} = -\frac{Q_{\text{diff}}}{T_2} \neq 0$$

The quantity of heat Q_{diff} is positive, therefore

$$\oint \left(\frac{\delta q}{T}\right)_{\text{irr}} < 0 \quad \text{-----} \quad (2)$$

combining eqns (1) and (2) to get clausius inequality

$$\boxed{\oint \frac{\delta q}{T} \leq 0} \leftarrow \text{clausius inequality valid for all cycles}$$

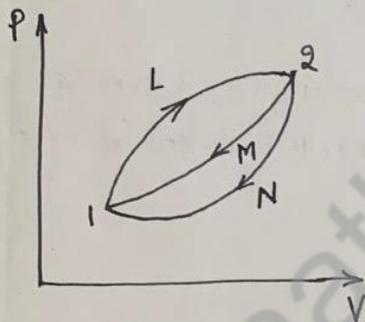
For Any machine $\oint \frac{\delta q}{T} > 0$ is impossible

$\oint \frac{\delta q}{T} = 0$, the cycle is reversible

$\oint \frac{\delta q}{T} < 0$, the cycle is irreversible

$\oint \frac{\delta q}{T} > 0$, the cycle is impossible

* Show that entropy, a property of the engine



Consider a system undergoing a reversible process from state 1 to state 2 along path 'L' and then from state 2 to the original state 1 along path 'M'

Applying the clausius theorem to the reversible cyclic process, we have

$$\oint_R \frac{\delta q}{T} = 0$$

When a system passes through the cycle 1-L-2-M-1, we have

$$\int_{1(L)}^2 \frac{\delta q}{T} + \int_{2(M)}^1 \frac{\delta q}{T} = 0 \quad \text{-----} \quad (1)$$

Now consider another reversible cycle, in which the system changes from state 1 to state 2 along path 'L', ~~but~~ but returns from state 2 to the original state 1 along a different path 'N'.

For the reversible process/cycle 1-L-2-N-1, we have

(5)

$$\int_{1(L)}^2 \frac{\delta Q}{T} + \int_{2(N)}^1 \frac{\delta Q}{T} = 0 \quad \text{--- (2)}$$

subtract equation (2) from eqn (1)

$$\int_{2(M)}^1 \frac{\delta Q}{T} - \int_{2(N)}^1 \frac{\delta Q}{T} = 0$$

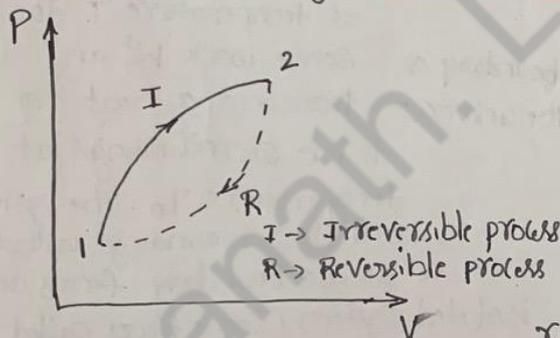
The quantity $\frac{\delta Q}{T}$ is a function of the initial and final states of the system and is independent of the path of the process. Hence it represents a property of the system. This property is called entropy.

Entropy is an extensive property defined by the equation

$$ds = \frac{\delta Q}{T}$$

$$\therefore \text{change in property } S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}$$

Entropy change for an irreversible process



consider a system undergoing a change from state 1 to state 2 by an irreversible process 1-I-2 and returns from state 2 to the initial state 1 by a reversible process 2-R-1 as

shown in fig.

For an irreversible process cycle, 1-I-2-R-1, the Clausius inequality can be written as

$$\oint_{1-I-2-R-1} \left(\frac{\delta Q}{T} \right) \leq 0$$

$$\text{or } \int_{1(I)}^2 \left(\frac{\delta Q}{T} \right) + \int_{2(R)}^1 \left(\frac{\delta Q}{T} \right) \leq 0 \quad \text{--- (1)}$$

For a reversible process, $\left(\frac{\delta Q}{T} \right) = ds$, the inequality (eqn 1)

reduces to

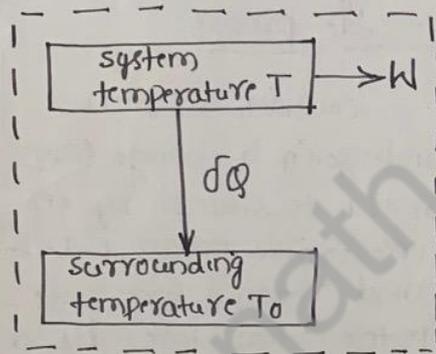
$$\int_1^2 \left(\frac{\delta q}{T} \right) + \int_2^1 ds \leq 0$$

$$\text{or } \int_1^2 \left(\frac{\delta q}{T} \right) + s_1 - s_2 \leq 0$$

$$\text{or } \boxed{s_2 - s_1 \geq \int_1^2 \left(\frac{\delta q}{T} \right)}$$

The equality sign stands for the reversible process and inequality sign stands for the irreversible process.

**** Principle of increase of entropy / entropy principle / change in entropy of the universe**



consider a system at temperature 'T' doing some work 'W' and transferring heat δq to the surroundings at temperature T_0 . The system and its surroundings within a single boundary forms an isolated system (some times called

as universe) as shown in fig.

Applying the principle of increase in entropy

$$(ds)_{\text{universe}} \geq 0$$

where $(ds)_{\text{universe}} = (ds)_{\text{system}} + (ds)_{\text{surroundings}}$

For the system, we have $(ds)_{\text{system}} \geq -\frac{\delta q}{T}$ (-ve sign indicates that heat is transferred from the system)

similarly for the surroundings, we have

$$(ds)_{\text{surroundings}} \geq \frac{\delta q}{T_0}$$

The total change in entropy for the combined system

$$(ds)_{\text{system}} + (ds)_{\text{surroundings}} \geq -\frac{\delta q}{T} + \frac{\delta q}{T_0}$$

$$\text{or } (ds)_{\text{universe}} \geq \delta q \left(-\frac{1}{T} + \frac{1}{T_0} \right)$$

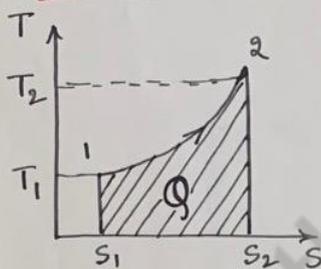
$$\text{but } T > T_0, \quad \therefore \left(-\frac{1}{T} + \frac{1}{T_0} \right) > 0$$

$$\boxed{(ds)_{\text{universe}} \geq 0} \leftarrow \text{This is the principle of increase of entropy.}$$

This equation indicates that the entropy of the universe is increasing continually.

** Entropy change during constant volume / Isochoric

Process:-



let 1 kg of gas be heated at constant volume and let the change in entropy and absolute temperature be from S_1 to S_2 and T_1 to T_2 respectively.

From 1st law of thermodynamics

$$Q = W + \Delta U$$

but $W = 0$ for constant volume process

$$\therefore Q = \Delta U$$

$$\text{but } Q = C_v (T_2 - T_1) \quad \left[\because du = \Delta U = C_v (T_2 - T_1) \right]$$

Differentiating

$$dq = C_v dT$$

Dividing both sides by T we get

$$\frac{dq}{T} = C_v \frac{dT}{T}$$

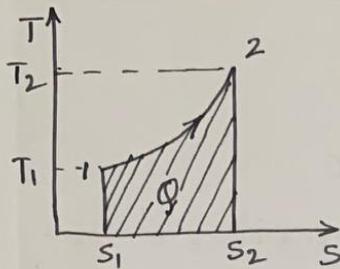
$$ds = C_v \frac{dT}{T}$$

$$\int_{S_1}^{S_2} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T}$$

Integrating both sides, we get

$$s_2 - s_1 = C_v \log_e \left(\frac{T_2}{T_1} \right)$$

* Entropy change during constant pressure / isobaric process



Let 1 kg of gas be heated at constant pressure, so that its absolute temperature changes from T_1 to T_2 and entropy s_1 to s_2 .

From 1st law of thermodynamics

$$\phi = W + \Delta U$$

$$\phi = Pdv + (U_2 - U_1)$$

$$= P(V_2 - V_1) + (U_2 - U_1)$$

$$= PV_2 - PV_1 + U_2 - U_1$$

$$= U_2 + PV_2 - U_1 - PV_1$$

$$\phi = h_2 - h_1 \quad (\because h = U + PV)$$

$$\phi = C_p(T_2 - T_1)$$

differentiating $d\phi = C_p dT$

dividing throughout by T , we get

$$\frac{d\phi}{T} = C_p \frac{dT}{T}$$

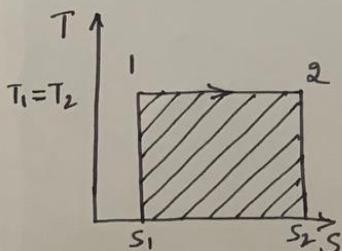
$$ds = C_p \frac{dT}{T}$$

Integrating both sides, we get

$$\int_{s_1}^{s_2} ds = C_p \int_{T_1}^{T_2} \frac{dT}{T}$$

$$s_2 - s_1 = C_p \log_e \left(\frac{T_2}{T_1} \right)$$

** Entropy change during isothermal process



An isothermal expansion 1-2 at constant temperature T is shown in fig. Entropy changes from s_1 to s_2 when gas absorbs heat during expansion. The heat taken by the gas is given by the area under the line 1-2 which also represents

(9)

the work done during expansion.

$$\text{i.e. } Q = W$$

$$\text{but } ds = \frac{dq}{T} \Rightarrow dq = T ds$$

Integrating on both sides

$$Q = \int_{s_1}^{s_2} T ds$$

$$Q = T(s_2 - s_1) \quad \text{and}$$

$$W = P_1 V_1 \log_e \left(\frac{V_2}{V_1} \right)$$

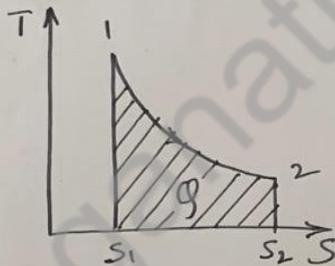
$$= RT_1 \log_e \left(\frac{V_2}{V_1} \right) \quad (\because P_1 V_1 = RT_1)$$

then

$$T(s_2 - s_1) = RT_1 \log_e \left(\frac{V_2}{V_1} \right)$$

$$\therefore \boxed{s_2 - s_1 = R \log_e \frac{V_2}{V_1}} \quad (\because T_2 = T_1 = T)$$

Entropy change during a polytropic process



Let 1 kg of gas at pressure P_1 , volume V_1 , absolute temperature T_1 and entropy s_1 be heated such that its final pressure, volume, absolute temperature and entropy are P_2 , V_2 , T_2 and s_2 respectively.

From 1st law of thermodynamics

$$Q = W + \Delta U$$

$$\text{i.e. } dq = dw + du$$

where dq = small change of heat

du = small change of internal energy

dw = small change of work done (Pdv)

$$\text{Now } dq = du + Pdv$$

$$dq = C_v dT + Pdv$$

Dividing throughout by T

$$\frac{dq}{T} = C_v \frac{dT}{T} + \frac{P}{T} dv$$

$$\text{but } \frac{dq}{T} = ds$$

$$\text{Also we have } PV = RT \quad \therefore \frac{P}{T} = \frac{R}{V}$$

$$\therefore ds = C_v \frac{dT}{T} + \frac{R dv}{V}$$

Integrating both sides, we get

$$\int_{s_1}^{s_2} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{V}$$

$$(s_2 - s_1) = C_v \log_e \left(\frac{T_2}{T_1} \right) + R \log_e \left(\frac{V_2}{V_1} \right) \quad (1)$$

$$\text{We have } P_1 V_1^n = P_2 V_2^n$$

$$\therefore \frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^n \quad (2)$$

$$\text{Also, we have } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right) \left(\frac{T_1}{T_2} \right) \quad (3)$$

From eqns (2) and (3), we have

$$\left(\frac{V_2}{V_1} \right)^n = \left(\frac{V_2}{V_1} \right) \left(\frac{T_1}{T_2} \right)$$

$$\left(\frac{V_2}{V_1} \right)^{n-1} = \left(\frac{T_1}{T_2} \right)$$

$$\therefore \frac{V_2}{V_1} = \left(\frac{T_1}{T_2} \right)^{\frac{1}{n-1}} \quad (4)$$

substituting eqn (4) in eqn (1)

$$(s_2 - s_1) = C_v \log_e \left(\frac{T_2}{T_1} \right) + R \log_e \left(\frac{T_1}{T_2} \right)^{\frac{1}{n-1}}$$

$$= C_v \log_e \left(\frac{T_2}{T_1} \right) + R \left(\frac{1}{n-1} \right) \log_e \left(\frac{T_1}{T_2} \right)$$

$$= C_v \log_e \left(\frac{T_2}{T_1} \right) - R \left(\frac{1}{n-1} \right) \log_e \left(\frac{T_2}{T_1} \right)$$

(11)

$$\begin{aligned}
&= C_v \log_e \left(\frac{T_2}{T_1} \right) - (C_p - C_v) \frac{1}{(n-1)} \log_e \left(\frac{T_2}{T_1} \right) \quad [\because R = C_p - C_v] \\
&= C_v \log_e \left(\frac{T_2}{T_1} \right) - (\gamma C_v - C_v) \frac{1}{n-1} \log_e \left(\frac{T_2}{T_1} \right) \quad [\because C_p = \gamma C_v] \\
&= \log_e \left(\frac{T_2}{T_1} \right) \left[C_v - (\gamma C_v - C_v) \frac{1}{(n-1)} \right] \\
&= C_v \left(1 - \frac{\gamma-1}{n-1} \right) \log_e \left(\frac{T_2}{T_1} \right) \\
&= C_v \log_e \left(\frac{T_2}{T_1} \right) \frac{n-1-\gamma+1}{n-1} \\
&= C_v \log_e \left(\frac{T_2}{T_1} \right) \frac{n-\gamma}{n-1} \quad \text{Per Kg of gas}
\end{aligned}$$

$$\boxed{S_2 - S_1 = C_v \left(\frac{n-\gamma}{n-1} \right) \log_e \frac{T_2}{T_1}}$$

Note:- Heat absorbed approximately equals the product of change of entropy and mean absolute temperature

$$\text{i.e. } \boxed{Q = (S_2 - S_1) \left(\frac{T_1 + T_2}{2} \right)}$$

Available and unavailable Energy

Available energy is that portion of the amount of heat energy supplied to a reversible engine, which could be converted into useful work.

The unavailable energy is that portion of energy which cannot be converted into useful work by any means.

Dead state :-

If the state of a system is brought close to the atmosphere, the opportunity for developing work diminishes and ceases completely, when the system reaches thermodynamic equilibrium with the atmosphere. This state of the system is called the dead state.

IDEAL GAS MIXTURE

Thermodynamics of Non-reactive Mixtures

Assumptions:

1. Each individual constituent of the mixture behaves like a perfect gas.
2. The mixture behaves like a perfect gas.
3. Individual constituents do not react chemically when the mixture is undergoing a process.

Mixture characteristics:

Consider a mixture of gases a, b, c, existing in equilibrium at a pressure P, temperature T and having a volume V.

The total mass of the mixture is equal to the sum of the masses of the individual gases, i.e., $m_m = m_a + m_b + m_c + \dots$ where subscript m = mixture, a, b, c = individual gases.

Mass fraction: The mass fraction of any component is defined as the ratio of the mass of that component to the total mass of the mixture. It is denoted by mf.

$$\text{Thus, } m_{fa} = \frac{m_a}{m}, \quad m_{fb} = \frac{m_b}{m}, \quad m_{fc} = \frac{m_c}{m}$$

$$\therefore m_{fa} + m_{fb} + m_{fc} + \dots = \sum_i m_{fi} = 1$$

Where the subscript i stands for the ith component. It shows that the sum of the mass fraction of all components in a mixture is unity.

Mole fraction: If the analysis of a gas mixture is made on the basis of the number of moles of each component present, it is termed a molar analysis. The total number of moles for the mixture is equal to the sum of the number of moles of the individual gases. i.e., $n_m = n_a + n_b + n_c + \dots$ where subscript m = mixture, a, b, c = individual gases.

(A mole of a substance has a mass numerically equal to the molecular weight of the substance, i.e., 1 kg mol of O₂ has a mass of 32 kg, 1 kg mol of N₂ has a mass of 28 kg, etc.) The mole fraction of any component is defined as the ratio of the number of moles of that component to the total number of moles. It is denoted by y.

$$\text{i.e., } y_a = \frac{n_a}{n_m}, \quad y_b = \frac{n_b}{n_m}, \quad y_c = \frac{n_c}{n_m}$$

$$\text{and } \therefore y_a + y_b + y_c + \dots = \sum_i y_i = 1$$

i.e., the sum of the mole fraction of all components in a mixture is unity.

The mass of a substance m is equal to the product of the number of moles n and the molecular weight (molar mass) M, or $m = nM$

For each of the components we can write,

$$n_m M_m = n_a M_a + n_b M_b + n_c M_c + \dots$$

Where M_m is the average molar mass or molecular weight of the mixture.

$$\text{Or } M_m = y_a M_a + y_b M_b + y_c M_c$$

Thus, the average molecular weight of a gas mixture is the sum of the products of all the components of the mole fraction and corresponding molecular weight of each component.

Note: Universal gas constant R MR where M = molecular weight, R : specific gas constant, and $R = 8.3143 \text{ kJ/kg-mole K}$

Where m_a = mass of gas "a", R_a = gas constant for gas "a", similarly $P_b V = m_b R_b T$

Partial Volume: Partial volume of a gas in a mixture is the volume occupied by the gas component at mixture pressure and temperature. Let V_a = partial volume of gas "a" and V_b = partial volume of gas "b".

$$\text{i.e., } P V_a = m_a R_a T \text{ \& } P V_b = m_b R_b T$$

The Gibbs-Dalton Law

Consider a mixture of gases, each component at the temperature of the mixture occupying the entire volume occupied by the mixture, and exerting only a fraction of the total pressure.

Applying the equation of state for this mixture we may write,

$$P_m V = m_m R_m T = n_m M_m R_m T = n_m R T$$

The above equation is known as the Gibbs Dalton Law of partial pressure, which states that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the individual components, if each component is considered to exist alone at the temperature and volume of the mixture.

Gas constant for the mixture:

$$\text{We have } P_a V = m_a R_a T$$

$$P_b V = m_b R_b T$$

$$\text{Or } (P_a + P_b) V = (m_a R_a + m_b R_b) T$$

Also, since the mixture behaves like a perfect gas,

$$\text{We have } P V = m R T \text{ --- (1)}$$

By Dalton's law of partial pressure, which states that, the pressure of mixture of gas is equal to the sum of the partial pressures of the individual components, if each component is considered to exist alone at the temperature and volume of the mixture.

$$\text{i.e., } P = P_a + P_b$$

The Amagat-Leduc Law: Expresses the law of additive volume which states that the volume of a mixture of gases is equal to the sum of the volumes of the individual components at the pressure and temperature of the mixture.

$$\text{., } V_m = V_a + V_b + V_c \dots P, T = V_i$$

$$\text{For Dalton law, } P_m = P_a + P_b + P_c + \dots V, T = P_i$$

PURE SUBSTANCE

A pure substance is one which has constant chemical composition throughout its mass. It may undergo phase change, but retains its chemical composition during a thermodynamic process.

Water, nitrogen, helium and CO₂ etc are the examples for the pure substance.

Water exists in three different phases, viz., solid as ice, liquid as water and vapour as steam. The chemical formula of water remains H₂O irrespective of the state.

Phase change of a pure substance (water)

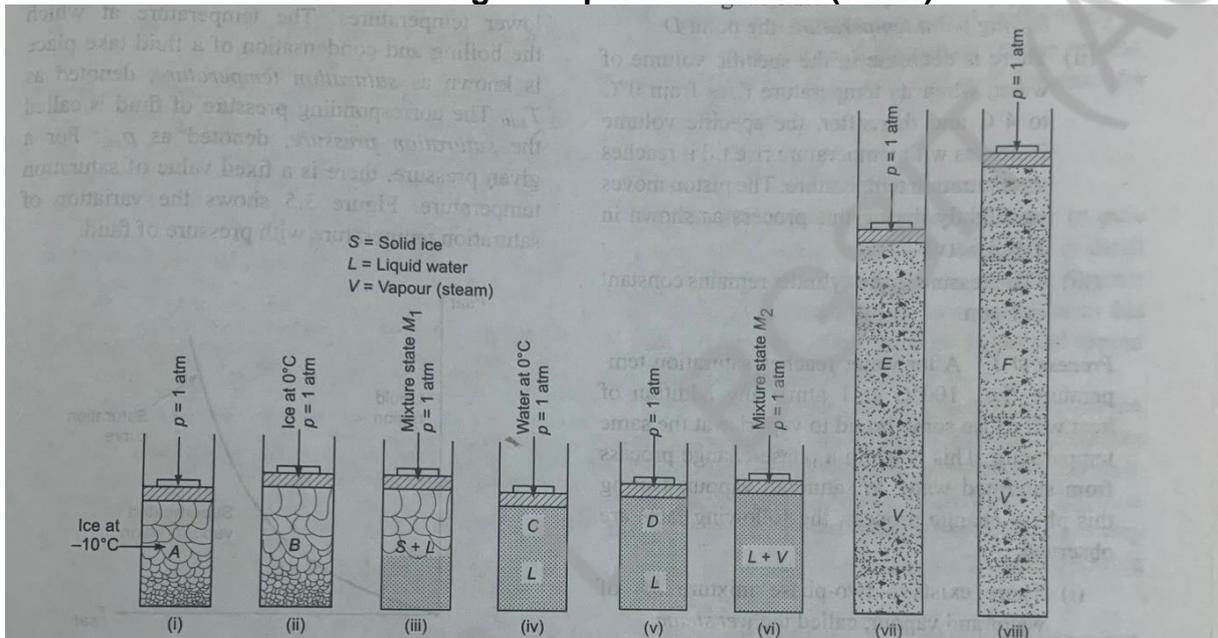
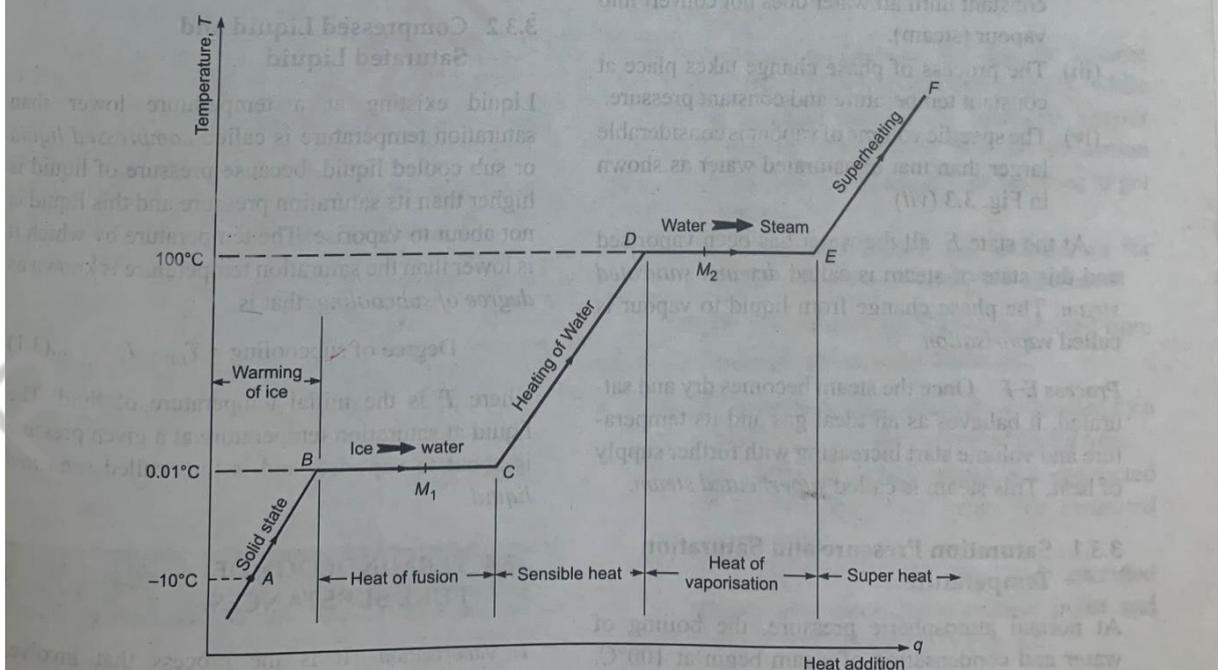


Fig. 3.3 Water in different thermodynamic states



Consider 1 kg of ice at -10°C taken in a cylinder fitted with free moving frictionless piston. A known weight is placed over the piston so that total weight of piston and placed weight exerts a required pressure 'p' of 1 atmosphere on the (ice/water/steam) substance throughout the experimentation.

The conditions of the substance and corresponding heat addition are shown in figures 1 and 2.

The stages of heat addition are explained briefly as below:

Process A-B: When certain amount of heat is added to the ice, it gets warmer and its temperature rises till 0.01°C i.e., 0°C at point 'B' as shown by the line AB.

Process B-C: Further ice begins to melt at 0°C and two-phase mixture is formed. The temperature of the mixture does not change with heat addition. At point 'C', all the ice melts to water at constant pressure and temperature, but slight decrease in volume of substance (water) in the cylinder.

Process C-D: The temperature of water rises with heat addition till the boiling point 'D' is reached and there is slight increase in volume. The temperature at which water begins to boil at given pressure is called *saturation temperature* denoted as ' T_s '.

Process D-E: Any addition of heat leads to the evaporation of water resulting in two phase mixture of water and steam called *wet steam* at saturation temperature at a given pressure. At point 'E', all the water has been vaporised and resulting in a *dry and saturated steam*. The volume increases slightly.

Process E-F: Further addition of heat to a dry steam at saturation temperature results in the formation of *superheated steam*. There is an increase in temperature above the saturation temperature at a given pressure is called *superheated temperature* denoted as ' T_{sup} '. There is a slight increase in volume.

Important terms related to steam formation

Latent heat of fusion: It is the quantity of heat required to convert 1 kg of ice into water at constant temperature of 0°C .

Saturation temperature: it is the temperature at which water begins to boil at a given pressure. It is denoted as ' T_s '.

Sensible heat: it is defined as the amount of heat required to raise the temperature of 1 kg of water at 0°C to the saturation temperature (T_s) at a given pressure. It is denoted as ' h_f '.

Latent heat of evaporation: It is defined as the amount of heat required to convert/evaporate 1 kg of water at saturation temperature (T_s) into 1 kg of dry steam at the same saturation temperature at a given pressure. It is denoted as ' h_{fg} '.

Amount of superheat: It is defined as the amount of heat required to raise the temperature of dry steam from its saturation temperature to any desired higher temperature at a given constant pressure. It is denoted by the relation ' $C_{ps} (T_{sup} - T_s)$ '.

Wet steam: It is a two-phase mixture of steam and water molecules in thermal equilibrium at the saturation temperature corresponding to a given pressure.

Dry saturated steam: The saturated steam at the saturation temperature corresponding to a given pressure having no water molecules in it is called *dry saturated steam*.

Superheated steam: The steam which is heated to a temperature higher than the saturation temperature at a given pressure is called *superheated steam*.

Degree of superheat: It is the difference between the superheating temperature and saturation temperature.

Enthalpy of dry steam: It is defined as the quantity of heat required to convert 1 kg of water at 0° C into 1 kg of dry steam at its saturation temperature at a given pressure. It is denoted as ' h_g '.

$$h_g = h_f + h_{fg} \text{ kJ/kg}$$

Enthalpy of wet steam: It is defined as the quantity of heat required to convert 1 kg of water at 0° C into 1 kg of wet steam at the specified dryness at its saturation temperature at a given pressure. It is denoted as ' h '.

$$h = h_f + x h_{fg} \text{ kJ/kg}$$

Enthalpy of superheated steam: It is defined as the quantity of heat required to convert 1 kg of water at 0° C into 1 kg of superheated steam at stated superheated temperature at a given pressure. It is denoted as ' h_{sup} '.

$$h_{sup} = h_f + h_{fg} + C_{ps} (T_{sup} - T_s) \text{ kJ/kg}$$

$$h_{sup} = h_g + C_{ps} (T_{sup} - T_s) \text{ kJ/kg}$$

where,

C_{ps} = Specific heat of superheated steam.

Dryness fraction: It is defined as the ratio of mass of the actual dry steam to the total mass of the wet steam. It is denoted as ' x '.

Dryness fraction, $x = \text{Mass of dry steam} / \text{Total mass of wet steam}$

$$x = m_g / (m_f + m_g)$$

Where m_f = Mass of water molecules.

Specific volume: It is the volume occupied by unit mass of a substance. It is expressed as m^3/kg .

Specific volume of saturated water: It is the volume occupied by 1 kg of water at saturation temperature at a given pressure. It is denoted as ' v_f '

Specific volume of dry steam: It is defined as the volume occupied by 1 kg of dry saturated steam at saturation temperature at a given pressure. It is denoted as ' v_g '

Specific volume of wet steam: It is defined as the volume occupied by the dry portion of steam in 1 kg of wet steam and volume occupied by water molecules in the same 1 kg of wet steam at saturation temperature at a given pressure. It is denoted as ' v '

$$v = x v_g + (1-x) v_f \text{ m}^3/\text{kg}$$

(1-x) v_f is very low at low pressure and often neglected.

Therefore,

$$v = x v_g \text{ m}^3/\text{kg}$$

Specific volume of superheated steam: It is defined as the volume occupied by 1 kg of superheated steam at saturation temperature at a given pressure. It is denoted as ' v_{sup} '

The superheated steam behaves like a perfect gas.

Therefore,

$$v_g / T_s = v_{sup} / T_{sup}$$

$$v_{sup} = (T_{sup} / T_s) * v_g \text{ m}^3/\text{kg}$$

where,

T_{sup} = Temperature of superheated steam in K.

T_s = Temperature of the saturated steam in K

External work of evaporation: It is defined as the fraction of latent heat of evaporation which does an external work.

External work of evaporation of dry steam = $P (v_g - v_f)$.

At low pressure, ' v_f ' is very small and can be neglected.

External work of evaporation of dry steam = $P v_g$, kJ/kg

External work of evaporation of wet steam = $P x v_g$, kJ/kg

External work of evaporation of wet steam = $P v_{sup}$, kJ/kg

where P is in KPa.

Internal latent heat: It is defined as the fraction of latent heat of evaporation required to change the phase.

Internal latent heat = Latent heat of evaporation – External work of evaporation

Internal latent heat of dry steam = $h_{fg} - P v_g$ kJ/kg

Internal latent heat of wet steam = $x h_{fg} - P x v_g$ kJ/kg

Internal energy of the steam: It is defined as the difference between the enthalpy of the steam and External work of evaporation.

Internal energy of the dry steam, $u_g = h_g - P v_g$ kJ/kg

Internal energy of the wet steam, $u = h - P x v_g$ kJ/kg

Internal energy of the superheated steam, $u_{sup} = h_{sup} - P v_{sup}$ kJ/kg

Throttling process: The process in which the fluid expands from high pressure to low pressure without doing any work and also there is no heat transfer.

Therefore,

Enthalpy before throttling = Enthalpy after throttling

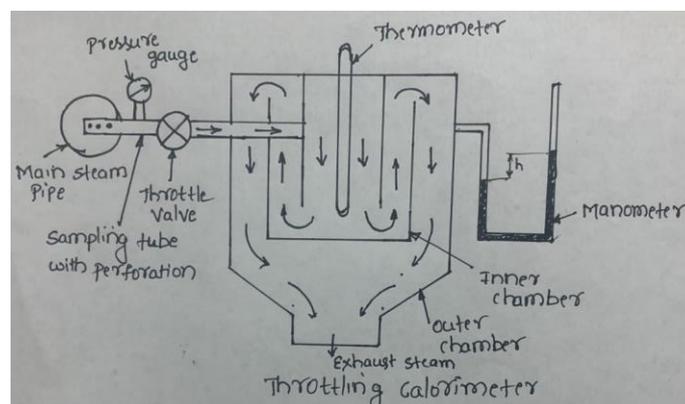
$$h_1 = h_2$$

Measurement of dryness fraction

Following are the devices used to measure the dryness fraction of a wet steam:

1. Tank or bucket calorimeter
2. Throttling calorimeter
3. Separating and throttling calorimeter.

Throttling calorimeter



The schematic diagram of a throttling calorimeter is shown in the above figure. A sample of wet steam at pressure P_1 whose dryness fraction to be measured is taken from steam main pipe through a perforated (i.e., small holes) sampling tube. The wet steam then expands through a throttle valve to a pressure P_2 and temperature T_2 . Due to larger pressure drop in the throttle valve, the steam becomes superheated and enthalpy remains constant during this throttling process.

The state 1 is defined by the pressure P_1 and dryness fraction x_1 . State 2 is defined by the pressure P_2 and temperature T_2 .

The enthalpy remains constant i.e., $h_1 = h_2$

At P_1 , $h_1 = h_{f1} + x_1 h_{fg1}$ (wet steam)

At P_2 , $h_2 = h_{g2} + C_{ps2} (T_{sup2} - T_{s2})$ (superheated steam)

Therefore,

$$x_1 = (h_2 - h_{f1}) / h_{fg1}$$

Where,

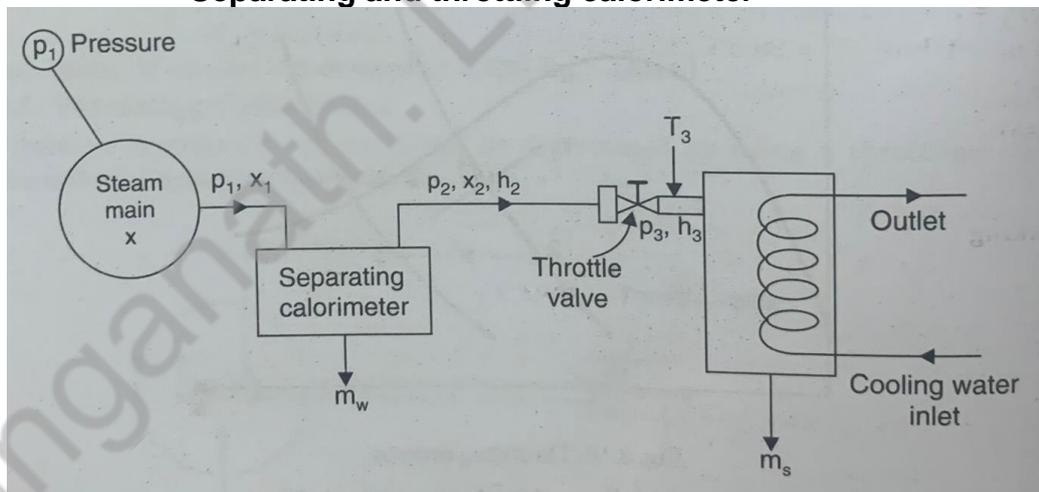
h_{f1} = Sensible heat of wet steam at P_1 kJ/kg

h_{fg1} = Enthalpy of evaporation at P_1 kJ/kg

h_2 = Enthalpy of superheated steam at P_2 and T_2

After throttling, steam is superheated at least by 5°C , then only good approximations are obtained from a throttling calorimeter. If the steam is very wet, the resultant dryness fraction is not very accurate.

Separating and throttling calorimeter



If the steam is very wet and the pressure after throttling is not low enough to take the steam to the superheated state, it is necessary to dry the steam partially before throttling by passing the steam through a separating calorimeter.

The schematic diagram of a separating and throttling calorimeter is shown in the above figure. Steam from the main is first enters the separator, where some part of the moisture separates out due to sudden change in the direction and falls by gravity. The quantity of water which is separated out (m_w) is measured at the separator. The partially dry steam which has higher dryness fraction is passed through the throttling calorimeter, where the steam is condensed after throttling to measure the amount of condensate (m_s).

Let,

m_w = Mass of water collected in separator, kg
 m_s = Mass of steam condensed after throttling, kg
 x_1 = Dryness fraction of steam after the separator.

The mass of dry steam leaving the separating calorimeter is equal to $(x_2 * m_s)$ = Mass of the dry vapour in the sample drawn from the main at state 1.

Dryness fraction in main, x_1 = Mass of dry vapour/Total mass = $(x_2 * m_s) / (m_w + m_s)$

Enthalpy before throttling at pressure P_2 = Enthalpy after throttling at pressure P_3

$$h_{f2} + x_2 h_{fg2} = h_3$$

where, $h_3 = h_{g3} + C_{ps3} (T_{sup3} - T_{s3})$

$$x_2 = (h_3 - h_{f2}) / h_{fg2}$$

Pressure – Temperature (P-T) diagram

The P – T diagram of a pure substance is generally called the phase diagram, as it shows solid, liquid and vapour regions of a pure substance simultaneously. The salient features of P -T diagram are as follows:

1. Each single phase of a pure substance is separated by saturation lines. The sublimation line separates the solid and vapour regions, the vaporisation line separates the liquid and vapour regions and the fusion line separates the solid and liquid regions.
2. The slope of the fusion line is negative that indicates that the melting point of ice decreases with increasing pressure.
3. The sublimation, fusion and vaporisation lines meet at a point called *triple point*; where all three phases of a substance coexist.

